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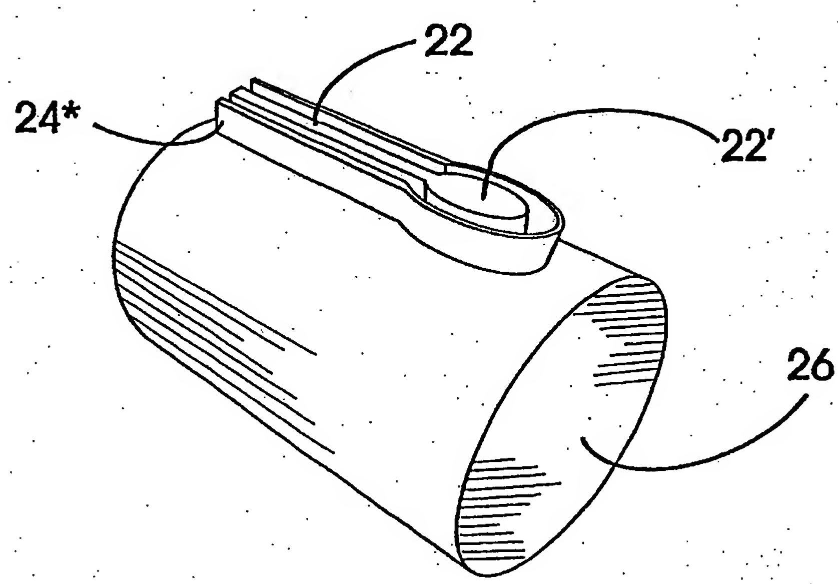


(57) Abstract

A sputtering magnetron with a rotating cylindrical target and a stationary magnet assembly (22, 24*) is described, said magnet assembly (22, 24*) being adapted to produce an elongate plasma race-track on the surface of said target, said elongate race-track having substantially parallel tracks over a substantial portion of its length and being closed at each end by end portions (22'), wherein the spacing between the tracks of said race-track is increased locally to materially effect sputtering onto a substrate. The increase in spacing may be at the end portions or along the parallel track portion. The increase in spacing may provide more even erosion of the target beneath the end portions of the race-track, provide more even coatings on the substrate, for instance.

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# MEANS FOR CONTROLLING TARGET EROSION AND SPUTTERING IN A MAGNETRON

The present invention relates to an improved rotating cathode magnetron suitable for sputtering or reactive sputtering of materials from a tubular cathode target onto a stationary or moving substrate as well as a method of operating the magnetron. The magnet assembly of the inventive magnetron is arranged in such a way that local variations in the plasma race-track are generated which may provide novel advantages to the sputtering process. In addition, the novel magnet assembly is particularly suitable for curvilinear arrangements.

## TECHNICAL BACKGROUND

In standard non-reactive metallic sputter mode, sputtering with planar magnetrons is known. The most important inconvenience is the formation of a groove of erosion in the target material, whereby this groove, and the plasma generating it, are often referred to as a "race track". The non-uniform erosion profile is inherently associated with the magnet configuration below the target. As a consequence, the target has to be replaced just before the erosion groove depth at any point equals the target thickness. Typically only 30% of the target material is consumed before the target has to be changed which makes it a very costly process because of labour costs, down time as well as the expense of target materials.

During reactive sputtering (i.e. the plasma contains one or more gases that will react with the target material) using planar magnetrons, additional problems of arcing and plasma instability are encountered. Both of these problems have been overcome by the introduction of cylindrical rotating target magnetrons. Firstly, with rotating target magnetrons no race track erosion profile (corresponding to the magnet configuration) is formed and the material consumption on the target can be up to 80%. Secondly, due to the nature of the rotating cathode, less problems and more stable processes are encountered during reactive sputter deposition. Nevertheless, large amounts of material are deposited on shields which are physically located between the target and the substrate to inhibit the deposition of target material on those locations where it is not desired. Therefore, regular cleaning and extensive precautions (e.g. water cooling) have to be foreseen on these shields

to reduce the risk of flaking. Flakes of material from shields can contaminate the sputtered surface.

Coating of large substrates in a uniform way during a single passage (i.e. typical condition in glass and web coating), is one of the most critical processes. Control may be obtained by placing additional wedge shaped shields (introducing another source of contaminating particle generation) or by changing the strength of the magnetic field lines (using magnets with different magnetisation or at different distances from the target). The latter solution may introduce non-uniform wear and/or consumption of the target material.

Cylindrical magnetrons have some other disadvantages which are typical for their geometry. The magnets are mounted on a static bar which is located within the rotating cylindrical target tube. The width of the magnet configuration is kept small which means that the turns at the end are quite sharp. Known magnet assemblies do not allow optimal configuration of the magnets in an end turn which results in reduced plasma confinement and increased electron loss at both ends of the target. It is desirable to have the magnets as close as possible to the target tube in order to produce the highest magnetic field strength at the surface of the cathode. In addition, at both ends of the target tube, where the magnets (and the race track) form a U-bend, more target material is removed. The top of the "U" - bend presents a length of the plasma race-track which remains at the same longitudinal position as the target rotates. This leaves a circular groove round the target tubes at both ends. Eventually, target life is limited by the depth of this groove as it is highly undesirable to deposit the underlying material of the tube onto the substrate.

Rotating cathode sputtering magnetrons with a stationary internal magnet assembly are known, e.g. from US 4,422,916, US 5,364,518 or WO 96/21750. In particular US 5,364,518 and WO 96/21750 propose magnet assemblies which produce an elongate plasma "race-track" above the target which has a shape comprising a spaced apart pair of parallel straight lengths terminated at each end by end portions or "U" turns. US Pat. No. 5,364,518 proposes controlling target erosion in the end portions by means of widening the track of the race-track in the end positions. As explained in WO 96/21750, the method according to US 5,364,518 has the disadvantage that the wider track of the race-track in the end portions may result in instability of the plasma due to the reduced field strength and resulting electron loss caused by the wider spacing of the magnets. Instead, WO 97/21750 proposes to make the end portions of the race-track "pointed", i.e. to elongate the end

portions into an acute angle, e.g. triangular or to make them semi-elliptical or parabolic in form. The disadvantage of making the end portions pointed, in particular triangular in shape is that the radius at the point is very small. This results in a high loss of electrons as they attempt to navigate this tight bend. To achieve reduce electron loss it may be considered to increase the magnetic field in this position in order to bind the electrons more closely to the track. However, increasing the magnetic field increases the plasma density and hence, the target erosion. Further, although WO 97/21750 proposes sophisticated geometrical shapes for the end portions of the race-track, e.g. parabolic or semi-elliptic, the only disclosed method of producing such refined track geometries is the use of discrete sections of magnets, the so-called "lumped" magnet method. It is not possible to accurately tailor the race-track to a sophisticated geometric form such as a parabola by means of lumped magnets - the steps between the magnets generate a castellated appearance which bears little relationship to a smooth curve (see Fig. 3 in the following).

US 5,645,699 describes the use of anodes to influence the deposition rate onto the substrate during reactive sputtering. This known method starts from the assumption that there is inevitable loss of electrons in the turns at the end of the race-track.

The present invention has the object of providing a sputtering magnetron and a method of operating the same which provides improved control over sputtering performance.

A further object of the present invention is to provide a sputtering magnetron and a method of operating the same which provides improved uniformity of erosion at the ends of the target.

Still a further object of the present invention is to provide a sputtering magnetron and a method of operating the same which provides improved uniformity of deposition onto the substrate.

Another object of the present invention is to provide a sputtering magnetron and a method of operating the same which provides a plasma race-track with reduced loss of electrons in the end portions thereof.

Yet a further object of the present invention is to provide a sputtering magnetron and a method of operating the same which provides improved target utilisation while allowing novel and useful ways of altering the coating sputtered onto the substrate.

## SUMMARY OF THE INVENTION

The present invention may provide a sputtering magnetron with a rotating cylindrical target and a stationary magnet assembly, said magnet assembly being adapted to produce an elongate plasma race-track on the surface of said target, said elongate race-track having substantially parallel tracks over a substantial portion of its length and being closed at each end by end portions, wherein the spacing between the tracks of said race-track is increased locally to materially effect sputtering onto a substrate.

The present invention also includes a method of operating a sputtering magnetron with a rotating cylindrical target and a stationary magnet assembly, comprising the steps of:

generating an elongate plasma race-track on the surface of said target using said magnet assembly, said elongate race-track having substantially parallel tracks over a substantial portion of its length and being closed at each end by end portions; and

increasing the spacing between the tracks of said race-track locally to materially effect sputtering onto a substrate.

The present invention may provide the advantage that the requirement for shields can be substantially reduced. As a consequence, the cost and time consuming maintenance of these shields can be lowered, while their detrimental effect on process and product quality can be minimised. This property can be achieved by reducing the unwanted deposition of material in the region between the target and the substrate. Though excess material is still brought into the vacuum system, it can be gathered at non-critical locations, e.g. on shields between the target and the chamber walls. These shields have no direct relation with the substrate and so require less precautions, less maintenance and have no effect on the process or film quality.

In addition, shields may no longer be needed to control the film thickness uniformity over (large) substrates. In addition, the current technology of changing magnet strengths and distances, resulting in non-uniform consumption of the target material can be overcome. Precise control of sputter efficiency towards the substrate for any desired position on the substrate can be obtained with the present invention, while maintaining uniform erosion of the cylindrical target tube. This means that standard tubes can be used for every possible uniformity of erosion profile.

Furthermore, the present invention allows freedom in the configuration of the

magnet assembly. The U-turns at the end of the target tube can be defined freely, allowing better control of the magnetic field. Therefore, plasma configurations in the turns and on straight zones can be achieved with which the loss of electrons is reduced. The radius of the U-turns can be varied even to values larger than the diameter of the target tube. In addition, in accordance with the present invention, the direction of magnetic field adjacent the magnet assembly may be arranged perpendicular to the target surface, allowing the creation of the largest possible magnetic field strength on the target surface. Likewise, the top surface of the magnets in the magnet assembly may be arranged parallel to the target tube which enables the closest possible positioning with respect to the target, giving the largest possible magnetic efficiency.

The circular erosion groove at the end of the target tube (due to the U-turns) known from conventional devices can be reduced and in some cases even be eliminated. A spoon or elliptical (i.e. more than semi-elliptical) shape is preferred for the race-track in the end zones in accordance with one embodiment of the present invention. Even old and worn targets, for which the groove is so deep that the underlying material becomes visible, can be used again without the risk of depositing the wrong material on the substrate.

In accordance with the present invention simultaneous metal and reactive sputtering can be achieved when the race-track is arranged to traverse the back side of the cathode.

The present invention also includes a sputtering magnetron having a magnet assembly and a target, said magnet assembly being adapted to produce a curvilinear plasma race-track on the surface of said target, said magnet assembly including: a first section for generating a magnetic field associated with a first magnetic polarity; a second section being spaced from said first section and generating a magnetic field associated with a second magnetic polarity, said first and second sections defining a magnetic field suitable for enclosing said curvilinear race-track; wherein one of the first and second sections includes at least one magnet and the other of said first and second sections is terminated by a soft magnetic material forming a magnetic circuit with said magnet. By the termination of the second section is meant that the second section defines the magnetic pole which is the interface between magnetic material and non-magnetic material, i.e. the atmosphere above the magnet array and the target.

The dependent claims define separate embodiments of the invention. The present invention, its embodiments and advantages will now be described with reference to the

following drawings.

**Brief Description of the Drawings**

Fig. 1 is a schematic representation of a rotating cathode sputtering magnetron in accordance with the present invention.

Figs. 2a and 2b show details of the magnetron of Fig. 1.

Figs. 3a to 3c show schematic respectively side, top and end representations of a conventional magnet assembly.

Figs. 4a to 4c show schematic respectively side, top and end representations of a magnet assembly in accordance with an embodiment of the present invention.

Figs. 5a to 5c show schematic respectively side, top and end representations of a magnet assembly in accordance with another embodiment of the present invention.

Fig. 6 shows an idealised race-track in an end-turn in accordance with an embodiment of the present invention.

Figs. 7A and B show graphs defining relationships to provide an erosion depth in the end turns of a magnetron in accordance with the present invention which is less than 20% greater than the erosion depth in the parallel central section.

Figs. 8A and B show graphs defining relationships to provide an erosion depth in the end turns of a magnetron in accordance with the present invention which is the same as the erosion depth in the parallel central section.

Figs. 9A to 9C show schematically a magnet assembly in accordance with another embodiment of the present invention.

Figs. 9D to F show the deposition profiles on the substrate achieved with the assembly shown in Figs 9A to C.

Fig. 10A shows a further race-track form in accordance with the present invention.

Figs. 10B and C show, respectively, the sputtered material efficiency and the layer thickness profile achieved with the magnet assembly of Fig. 10A

Figs. 11a to 11c are representations of the race-track form, sputtered efficiency and layer thickness profile for a conventional race-track.

Figs. 12A to 12C show further magnet assemblies in accordance with the present invention including soft magnetic materials.

Figs. 13 to 15 show further preferred magnet assemblies in accordance with the

present invention.

## DESCRIPTION OF THE ILLUSTRATIVE EMBODIMENTS

The present invention will be described with respect to particular embodiments and with reference to certain drawings but the invention is not limited thereto but only by the claims. The drawings described are only schematic and are non-limiting.

Figs. 1 and 2a and 2b are schematic views of the sputtering magnetron 10 in accordance with the present invention. Fig. 1 is a schematic side view of the target 4 within the vacuum chamber 2, whereas Fig. 2a is a schematic cross-sectional view through the target 4. Fig. 2b is an enlarged view of a part of the target 4 from Fig. 2a. Vacuum chamber 2 preferably includes a removable, cylindrical rotating target 4. The target 4 may be driven by any suitable drive means, e.g. an electric or hydraulic motor or similar linked to the target 4 through a feed-through 6. The other end of the target 4 may be supported by a further feed-through 8 through which cooling liquid for the target 4 and an electrical supply (not shown) may be brought into chamber 2. The target 4 may be a tube made from the material to be sputtered or may have on its outer surface a separate layer 5 of material to be sputtered. The target 4 is generally held at a negative potential by a voltage supplied through feed-through 8. Typical target materials may be, for example only, titanium or silicon. A substrate 12 to be sputtered is arranged adjacent the target 4. The substrate 12 may be stationary or may be a continuous sheet of material moved past the target 4, e.g. driven by rollers 11. Typical substrate materials may be, for example only, sheet glass, plastic web or sheet metal. The vacuum chamber 2 may also include means 14 for introducing an inert gas such as argon as well as means 16 for introducing further reactive gases e.g. Nitrogen or oxygen for reactive sputtering. Further, there may be more than one substrate 12 and more than one target 4 within the chamber 2.

A generally stationary magnet assembly 20 is arranged within the cylindrical target 4. The magnet assembly 20 may be made up of a collection of individual magnets 22, 24 arranged in a given pattern or may in accordance with one aspect of the present invention include magnets forming one polarity and a specially shaped soft magnetic material forming the other polarity. Generally, a central row or rows of magnets 22 having one polarity towards the target layer 5, e.g. north poles, is surrounded by a closed loop of either a soft magnetic material or magnets 24 which have the opposite polarity towards the target 4, e.g.

south poles. The magnets 22, 24 may advantageously be arranged on a soft magnetic former 26 as a keeper, which former 26 may advantageously be tubular or part of a tube. Further, magnets 22, 24 may be preferably inserted into a plastic tube 21 which prevents oxidation of the magnets 22, 24 and surrounded by a further tube 19 to prevent contact with cooling fluid.

In operation, the intense magnetic field 17 generated by the magnets 22, 24 just above the target material 5 in combination with the crossed electrostatic field between the target 4 and the substrate 12 generates a closed loop of plasma discharge which sputters material from the surface 5 of the target 4 towards the substrate 12. Heat generated by the sputtering is removed by a cooling circuit, e.g. cooling fluid circulated through a space 25 below the target layer 5 and supplied by a central tube 23. For conventional metal sputtering or for reactive sputtering, a vacuum of $10^{-2}$ to $10^{-4}$ mbar is preferably maintained in the vacuum chamber 2.

In accordance with the present invention, the magnet assembly 20 of a sputtering magnetron 10 with a rotating cylindrical target 4 is adapted to produce an elongate plasma race-track on the surface of the target 4 (see Fig. 11A), the elongate plasma race-track having substantially parallel tracks over a substantial portion of its length and being closed at each end by end portions, wherein the track spacing of the race-track is varied locally to materially effect sputtering onto a substrate.

A conventional magnet configuration in a rotating magnetron is depicted in Fig. 3 for comparison as is known for instance from WO 97/21750. The drawing shows only one end of the target tube 4, the other end has a similar arrangement. The central magnets 22 (shown as a double bar) have the opposite magnetisation direction with respect to the surrounding magnets 24, 24', 24" and 24'". The magnetic field distribution obtained includes a substantially parallel central portion 28 and the magnets 24', 24", 24'" nearest to the tube end create the closed end loop 29. Fig. 3b is a schematic top view of the magnet array 20. The magnet array 20 is shown as including continuous straight magnets 22 however it should be understood that the magnet array 20 may be made up of a series of individual magnet blocks arranged in a line which may be called a "lumped" magnet array. The lumped magnets 24', 24", 24'" create a magnetic field which includes series of steps and approximates a smooth curve such as a parabola or semi-ellipse very badly. Fig. 3A shows a longitudinal cross-sectional schematic representation of the conventional magnet array

20. The outer loop formed by magnets 24', 24", 24''' appears offset with respect to the inner magnets 22 because of the curvature of the cylindrical support of the magnet array 20 (not shown). Fig. 3C is a schematic cross-sectional end view through the target tube 4.

Examples of the magnet assembly in accordance with the present invention will be described with reference to Figs. 4 to 11. In Figs. 4 and 5, the end portions 29 of the magnet array 20 are increased in diameter 34 compared with the width 33 of the substantially parallel central portion 28. This can be used to control the erosion of the target 4 in the end regions. In Fig. 9 the spacing 35 of the magnet array 20 in a section of the parallel central portion 29 is increased. This changes the direction of sputtering locally which may be used to produce special effects, e.g. reducing the thickness of the coating sputtered onto a substrate 12. In Fig. 10, the local spacing of end portions 29 of the magnet array 20 has been increased locally to alter the amount of material sputtered to the substrate 12 from the corresponding zones of the target 4.

In Figs. 4 a-c only one end of the target tube 4 is shown, the other end may have a similar or a different arrangement. Fig. 4 is a schematic idealised representation of a magnet assembly 20 in accordance with one embodiment of the present invention. The central magnets 22 (shown as a double bar) have the opposite magnetisation direction (e.g. north poles towards the target) with respect to the surrounding magnets 24. The magnetic field distribution obtained includes a substantially parallel central portion 28 and the magnets nearest to the tube end create the closed end loop 29. Fig. 4B is a schematic top view of the magnet array 20 in accordance with one embodiment of the present invention. The magnet array 20 is shown as a continuous line 22, 24, however it should be understood that the magnet array 20 may be made up of a series of individual magnet blocks or may include a specially shaped soft magnetic material as one polarity or both polarities. Fig. 4A shows a longitudinal cross-sectional schematic representation of the magnet array 20. The magnets 22, 24 of the magnet array 20 are arranged close to the inner diameter of the target tube indicated by 4. The magnets 22, 24 may advantageously be mounted on a soft magnetic tube 26 (shown best in Fig. 4c) or part of a tube, e.g. pure iron or mild steel. The inner magnets 22 form a loop 25 at the end 29 which may have a diameter larger than or equal to the width of the double bar towards the centre of the target 4. Loop 25 may be replaced by a single magnet in the same position (not shown) having a shape identical to the shape of the loop 25. The outer magnets 24 also form a loop 27 at the end of a parallel central

section 28. Loop 27 may have a diameter 34 larger than or equal to the width 33 of the central section. The spacing between the outer magnets 24 and the inner magnets 22 in the central substantially parallel region is indicated by 31. The spacing 32 of the outer loop 27 and the inner loop 25 of magnets 24, 22 in the end loop region 29 may be equal to the spacing 31 or may be different, e.g. greater, and may vary around the loop region 29. In accordance with the present invention the spacing 32 and the diameter 34 may be arranged with a specific relationship to each other in order to improve the uniformity of the erosion of the target 4.

Due to the curvature of the target 4, portions 35 and 37 of the outer and inner loops 27, 25 in Fig. 4a appear offset with respect to the central and end portions 22, 24, 36, 38 thereof. Fig. 4C is a cross-sectional end representation through the target tube 4 showing the former 26.

Figs. 5 a -c show an alternative embodiment of the present invention. The reference numbers in Fig. 5 which are the same as those in Fig. 4 a-c represent similar components. In this embodiment, the inner and outer magnets 22, 24 in the end portion 29 extend around the inside of tubular target 4 so that the portions 36 and 38 of the outer and inner loops 27, 25 extend to the rear of the target away from the substrate 12. The effect of this magnet arrangement is that the plasma race-track follows the magnets 22, 24 around the back of the target, extending away from the substrate 12 resulting in target material being sputtered onto the inside of the vacuum chamber 2 rather than onto the substrate. In accordance with the present invention, the end loops 25, 27 may be set at any position between the two extremes shown in Fig. 4 and 5.

An application of the embodiments shown in Figs. 4 a-c and 5 a-c will be described with reference to Figs. 6 to 8. Fig. 6 shows a schematic representation of the end loop 49 of a plasma race-track 50 in accordance with the present invention. Magnets 22, 24 are arranged as shown in schematically in Fig. 4 or 5 to produce the plasma race-track 50. The end loop 49 may comprise three zones. A transition zone 52 may be provided between the central parallel portion 56 of the race-track and the end of loop 49. This transition zone 52 may include graceful swan-neck transitions on both sides of the race-track 50 avoiding sharp corners or changes of direction. Transition zones 52 may be dispensed with if the transition from the mid-zones 54 to the substantially parallel central section 56 of the race-track 50 is small. The mid-zones 54 may be approximated by arcuate sections. An end zone

58 which may be approximated by an arcuate section, joins the mid-zones 54 together. The width of the track "s" of the race-track 50 may vary around the end loop 49 but in accordance with the present invention this width "s" will be approximated as a constant width at least in the end zone 58. The width of the track of the race-track varies in the mid- and transition zones 54, 52 smoothly from "s" in the end zone 58 to the width "t" in the central section 56 of the race-track 50. It will be assumed that, at least approximately, the arcuate sections of the mid- and end zones 54, 58 join tangentially, i.e. without discontinuity. Further, it will be assumed that the race-track form provided by the transition zones, mid-zones and end zones, 52, 54, 58 may be approximated to an ellipse with a parallel radius "r" and a perpendicular radius "p". As is well known an ellipse may be represented by the formula:

$1 = x^2/r^2 + y^2/p^2$ where y is the vertical axes and x the horizontal one.

It will be understood by the skilled person that these approximations are made to define the present invention and that the present invention includes plasma race-tracks and their corresponding magnet arrays which achieve the same effects as will be described for the present invention even if the magnet array and the corresponding plasma race-track differs somewhat from the idealised representation shown in Fig. 6.

In accordance with the present invention it has been determined that for particular relationships between "r", "s" and "p" in combination with magnet strengths and materials as well as the distance the magnets are placed from the target, the erosion of the target around end loop 49 may be substantially uniform. Substantially uniform in accordance with the present invention means less than 20% differences in target erosion around the end loop 49 and between the end loop 49 and the central portion 56 of the race-track. The present inventor has determined the surprising fact that there are combinations of "r", "s" and "p" in combination with the magnet strengths and materials and the distance from the magnets to the target with which the radii in the end loop 49 can be relatively large and the field strength sufficiently high making it easier for the electrons to traverse the curve without exiting from the plasma while still being able to keep the magnetic field in these curves such that the target erosion depth can be controlled. Due to the use of gentle curves with large radii in the turn region 49 combined with a change in track width of the race-track in the turn and/or a reduction in the intensity of the magnetic field, the erosion is not only uniform

but also the electron loss is reduced to a minimum.

Figs. 7A and B show certain limiting results for a maximum of 20% difference in erosion depth around the end portion 49 of the race-track or between the end portion 49 and the substantially parallel central section 56, i.e. 20% difference or less (down to no or 0% difference) which is "substantially uniform erosion" in accordance with the present invention. Figs. 8A and B show similar graphs for 0% difference in target erosion. The "y" axis in Figs. 7 and 8 relates to the average target erosion rate per unit width of erosion groove compared to the parallel centre section ( 1 = the same rate per unit width as in the central section). The "x" axis is the ratio of p/r for the elliptical approximation of Fig. 6. The third (z) dimension in Figs. 7A and 8A is representative of the width of the target erosion profile "s" (similar to but not the same as the magnet spacing). It has been found by the present inventor that the width of the race-track in the turn which gives substantially uniform erosion is given by z x p as an approximation. As an example from the graph Fig. 7A, if the ratio of groove erosion per unit groove width (y axis) is 1 (i.e. the erosion rate per unit groove width in the turn is the same as in the parallel central region), and the ratio of p/r is 1.5, the z co-ordinate is 2.8. Accordingly, the erosion groove width in the centre of the turn should be set to z.p = 2.8p or 4.2r to obtain substantially uniform erosion.

The graphs of Figs. 7A and 8A, therefore, define iso-erosion surfaces, i.e. those of relatively uniform erosion. Any co-ordinate lying in or between the iso-erosion surfaces defined in Figs. 7A and 8A will provide an erosion depth within the range +20% and 0% compared to the erosion depth in the central parallel section of the race-track, i.e. end turns with a substantially uniform erosion in accordance with the present invention.

As explained above it is preferred in accordance with the present invention if there are only gradual changes in the race-track direction in the end portion 49. A very large or small p/r ratio means that the electrons in the plasma must follow a rapidly changing path including tight bends which is conducive to loss of electrons from the plasma. It is preferred if the ratio of p/r is less than 2. It is also preferred if the erosion groove width is less than 1.5r, more preferably less than 1.2r. Substituting the erosion groove width = z.p, these restrictions result in the dimension z being preferably smaller than 1.5r/p and more preferably 1.2r/p. These limits are shown in Figs. 7B and 8B. The right hand solid line relates to the restriction $z \leq 1.5r/p$ and the left hand dotted line relates to $z \leq 1.2r/p$. Figs 7A, B and 8A, B have the same x and y axes - in Figs. 7B and 8B the details of Figs. 7A

and 8A have been omitted for clarity purposes. These restrictions may also place a maximum on p/r of about 1.75. It is more preferred if the ratio of p/r is less than 1.5, and it is also preferred if p/r approaches about 1, i.e. close to a circle. Further, the larger the value of r/p the longer the end loop 49 becomes, thus taking up space at the ends of the target and making the design of the magnet arrangement more difficult. Hence, it is preferred if r/p is less than or equal to 5. If all these limitations are included they define a region in Figs. 7A and 8A in which acceptable turn geometries may be obtained. This acceptable region may be defined as: $0.2 \leq p/r \leq 2$, more preferably $0.4 \leq p/r \leq 1.75$ and most preferably $0.6 \leq p/r \leq 1.5$. These regions define an end loop 49 which is rather spoon-shaped.

Figs. 9 a-e are schematic representations of a further embodiment in accordance with the present invention. Reference numbers in Figs. 9 a-e which are the same as in Figs. 4 and 5 refer to similar components. Figs. 9 a-c show top-view representations of a part of the central substantially parallel section 28 of the magnet array 20. At least in a portion of the substantially parallel section 28, the magnet tracks 22, 24 are widened to an overall width of 35 which is larger than the width 33 of the adjacent section. The width 31 between the magnets 22, 24 may remain the same. The effect of this local variation is portrayed schematically in Figs. 9d and 9e. In the section having an overall width 33, as shown in Fig. 9a, the sputtering direction is mainly perpendicular to the substrate 12. This results in a localised thick sputtered layer 42 on substrate 12. As substrate 12 is moved in a direction perpendicular to the axis of the target 4, the coating 40 is deposited along the length of substrate 12. As shown schematically in Fig. 9e, the direction of sputtering created by the wider width 35 magnet array 20 is inclined at an angle to a perpendicular to the substrate 12. This results in a flatter deposition profile 42 on the substrate 12. Further, some of the sputtered target material may not reach the substrate 12 but is sputtered onto the inside of the vacuum chamber 2 or more preferably onto further, rotating targets arranged on each side of target 4 (not shown) and parallel thereto. The average erosion of the rotating target 4 remains the same in both the situations depicted in Figs. 9d and 9e. The longitudinal thickness profile of the deposited layer 42 is shown in Fig. 9f. This example shows a symmetrical spacing although the present invention is not limited thereto.

Figs. 10 a-c are schematic representations of yet another embodiment in accordance with the present invention. Reference numbers in Figs. 10 a-c which are the same as in Figs. 4 and 5 represent similar components. In this embodiment, one or more asymmetrical

protrusions of the magnet array 20 are provided adjacent the end of the substantially parallel portion 28, just before or within the end loop region 29 in order to produce local protrusions 44 in the race-track. The effect of these protrusions 44 is to increase locally the amount of sputtered material from the target 4 to the substrate 12, i.e. to increase the deposition rate locally.

An application of the embodiment shown in Figs. 10 a-c will be compared with reference to Fig. 11. In Fig. 11a a conventional elongate race-track 59 for a rotating cathode magnetron is shown. In Fig. 11b the conventional target erosion profile for the race-track of Fig. 11a is shown. The erosion is deeper at the ends of the race-track 59 in the turn. Fig. 11c shows the deposition layer thickness on the substrate 12. Due the fact that the sputtering is not perfectly perpendicular to the target 4 but is distributed over an angle, the deposition rate at the ends of the race-track is reduced as some of the target material is sputtered away from the substrate. This results in a lowering of the deposition thickness at the ends of the target.

The target erosion profile and deposition thickness profile produced with the arrangement shown in Fig. 11a is shown in Figs. 11b and 11c respectively. By adding the protrusions 44, the amount of material deposited at the ends of the race-track is increased resulting in a more square deposition profile in Fig. 11c. On the other hand the length of target having increased target erosion is also increased as shown in Fig. 11b. The increased target erosion can be compensated by using replaceable end-pieces for the target 4 which are replaced more often than the central region of the target or by increasing the material thickness of the target at the ends thereof.

In the embodiments of the invention described with reference to Figs. 4 to 11, the magnet assembly 20 has been shown as if formed from a smooth curvilinear structure. In accordance with the present invention, the magnet assembly 20 may be formed by lumped magnets. It is preferred in accordance with the present invention if the commercially available high powered, hard and generally brittle and almost unworkable magnets conventionally used in magnetrons are combined with specially shaped soft magnetic materials such as iron to provide enhanced curvilinear geometries for the magnetic assembly 20. Soft magnetic materials, e.g. soft iron, in combination with permanent magnets may be used in accordance with the present invention in magnetrons generally and this advantageous combination is not limited to rotating target magnetrons.

Examples of suitable combinations of magnets and soft magnetic materials are shown schematically in Figs. 12 to 15. Figs. 12A to C show three schematic and illustrative examples of such suitable magnet arrangements in cross-section. Each consists of at least one permanent magnet 60 and a soft magnetic material 62. As shown in Fig. 12A, an electromagnet or a permanent magnet 60 may be placed inside and in contact with a U-shaped soft magnetic material 62. The central magnet 60 has one pole, e.g. the north pole, directed upwards towards the target and the other poles are generated by the soft magnetic material 62. Such an arrangement can replace two rows of conventional magnets. As shown in Fig. 12B, the magnet 60 may be placed between two soft magnet forms 62, 64, e.g. two U-shaped channels of differing sizes, thus replacing two rows of conventional magnets. Fig. 12C shows three permanent magnets 60, 66, 68 and a shaped soft magnet 62 forming intermediate poles. Such a magnet array can create a plurality of plasma zones generated by the magnetic field between the various pairs of north and south poles.

The advantages of the use of shaped soft magnetic materials are as follows:

1) The volume and/or number of permanent magnets can be reduced to about half of that used conventionally.

2) The array or arrays of permanent magnets can be mounted easily on the soft magnetic material which itself can be easily secured to the magnetron. The sides of the soft magnet materials are rigid and integral with the rest so that no special fixing or stabilisation is required therefore.

3) Curvilinear race-tracks can be generated more easily and more precisely. The soft magnetic material, e.g. soft iron, can be machined, forged, welded etc. and can take on any desired shape. This allows smooth bends and turns rather than the castellated turns of conventional arrangements. This allows more complex race-track shapes such as ellipses or parabolas. The central permanent magnet may remain in the lumped form but it is easier to create a suitable central form with lumped magnets than a smooth outer form.

4) The soft magnetic material may be segmented at appropriate places and the segments driven back and forwards allowing dynamic modification of the race-track form.

The present invention includes modifications to the basic structures shown in Figs. 12A to C which are non-limiting. For instance, the spacing between the pole or poles generated in the soft magnetic material and the pole or poles of the permanent magnets can be varied at will. Further, the height of the vertical sections of the soft magnetic material

can be changed at will to modify the magnetic field generated.

Fig, 13 shows part of a preferred arrangement for the magnet assembly shown schematically in Fig. 4. The central permanent magnet array 22 is provided by a series of rectangular magnets arranged in a line terminated by a substantially circular or elliptical magnet 22' to form the end turn. These magnets are secured to an outer U-shaped soft magnetic material 24* which is shaped to provide the outer poles 24, in particular a smooth turn at the ends. The soft magnetic material 24* is secured to the support cylinder 26.

Fig. 14 shows part of a preferred arrangement of the magnet assembly shown in Fig. 5. The end turn is very large in size and the race-track goes right around the target cylinder in the end turn. A single line of permanent magnets 22 are secured within a U-shaped soft magnetic former 24* which provides the other pole 24. The soft magnetic material 24* is fixed to the support tube 26 which is shown transparent for clarity purposes. As the radii are very large, the gaps between the discrete permanent magnets 22 are small. The individual magnets making up the line 22 may be set into specially machined flat sections of the base of soft magnetic material 24* in order to reduce edges and discontinuities between the magnets of lines 22 caused by the curvature of tube 26. This configuration creates a double closed race-track (one inside the other) with opposite electron movement.

Fig. 15 shows an end part of a preferred arrangement for the magnet assembly shown schematically in Fig. 10. Permanent magnets 22 are arranged in a line to generate, in combination with outer U-shaped soft magnetic material 24* a central substantially parallel section of the race-track 50 Further permanent magnets 22* are arranged perpendicular to the main central portion 22. These magnets are placed within a U-shaped soft magnetic former 24* having graceful outer curves, generating a race-track of the form shown in Fig. 10A with local protrusions 44 near the ends.

While the invention has been shown and described with reference to preferred embodiments, it will be understood by those skilled in the art that various changes or modifications in form and detail may be made without departing from the scope and spirit of this invention.

## Claims

1. A sputtering magnetron with a rotating cylindrical target and a stationary magnet assembly, said magnet assembly being adapted to produce an elongate plasma race-track on the surface of said target, said elongate race-track having substantially parallel tracks over a substantial portion of its length and being closed at each end by end portions, wherein the spacing between the tracks of said race-track is increased locally to materially effect sputtering onto a substrate.

2. The magnetron according to claim 1, wherein said magnet assembly further comprises: an elongated central section positioned within said cylindrical target and generating a magnetic field associated with a first magnetic polarity; a peripheral section positioned within said cylindrical target and being arranged around said elongated central section such that spaces are defined between said peripheral section and said elongated central section, said peripheral section generating a magnetic field associated with a second magnetic polarity; wherein said elongated central section and said peripheral section define a magnetic field suitable for enclosing said racetrack; and wherein said magnetron further comprises: means for causing relative rotation between the cylindrical target and said magnet assembly.

3. A magnetron according to claim 2 wherein each said end portion of the plasma race-track is representable substantially by an ellipse with a radius "p" and "r" in the directions perpendicular and parallel to the parralel track portion, respectively and the width of the track of the race-track in at least the middle of an end portion being represented by "s", the dimensions "s", "p" and "r" being chosen in a pre-determined relationship to each other in combination with the magnet field strengths and magnetic materials used in said central section and/or said peripheral section of the magnet assembly and the distance between the central and/or the peripheral section and the target to render the target erosion in the end portion substantially uniform.

4. A magnetron according to claim 3 wherein the width of the erosion groove caused by the race-track in the target is less than 1.5r.

5. A magnetron according claim 3 or 4, wherein the ratio p/r is defined by $0.2 \leq p/r \leq 2$,. more preferably $0.4 \leq p/r \leq 1.75$ and most preferably $0.6 \leq p/r \leq 1.2$.

6. A magnetron according to claim 1 or 2 wherein the end portions include local protusions of the plasma race-track.

7. A magnetron according to claim 6 wherein the protusions are arranged so that the deposition layer deposited on a substrate is more uniform in regions close to the end portions.

8. A magnetron according to claim 1 or 2, wherein the spacing between the tracks in the portion of the race-track having parallel tracks is varied locally.

9. A magnetron according to claim 8, wherein the spacing is varied so that a portion of the sputtered target material is sputtered onto a further rotating cylindrical target located adjacent to said rotating cylindrical target.

10. A magnetron according to any of the claims 2 to 9, wherein one of the central and peripheral sections includes at least one magnet and the other of the central and peripheral sections includes a soft magnetic material forming a magnetic circuit with said magnet.

11. A sputtering magnetron having a magnet assembly and a target, said magnet assembly being adapted to produce a curvilinear plasma race-track on the surface of said target, said magnet assembly including:
a first section for generating a magnetic field near said target associated with a first magnetic polarity;
a second section being spaced from said first section and generating a magnetic field associated with a second magnetic polarity, said first and second sections defining a magnetic field suitable for enclosing said curvilinear plasma race-track; wherein one of the first and second sections includes at least one magnet and the other of said first and second sections is terminated by soft magnetic material forming a magnetic circuit with said magnet.

12. A method of operating a sputtering magnetron with a rotating cylindrical target and a stationary magnet assembly, comprising the steps of:
generating an elongate plasma race-track on the surface of said target using said magnet assembly, said elongate race-track having substantially parallel tracks over a substantial portion of its length and being closed at each end by end portions; and
increasing the spacing between the tracks of said race-track locally to materially effect sputtering onto a substrate.

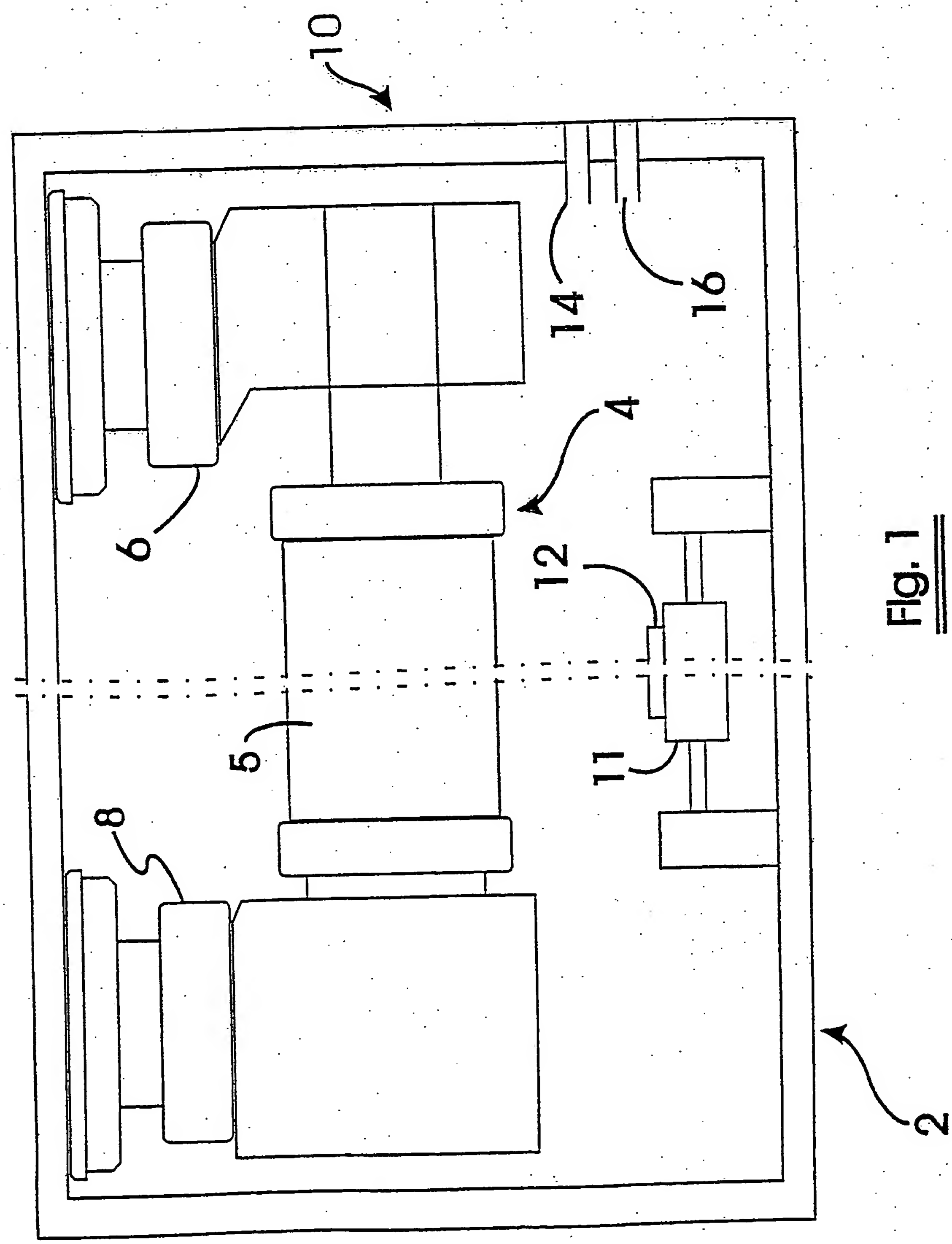



Fig. 1

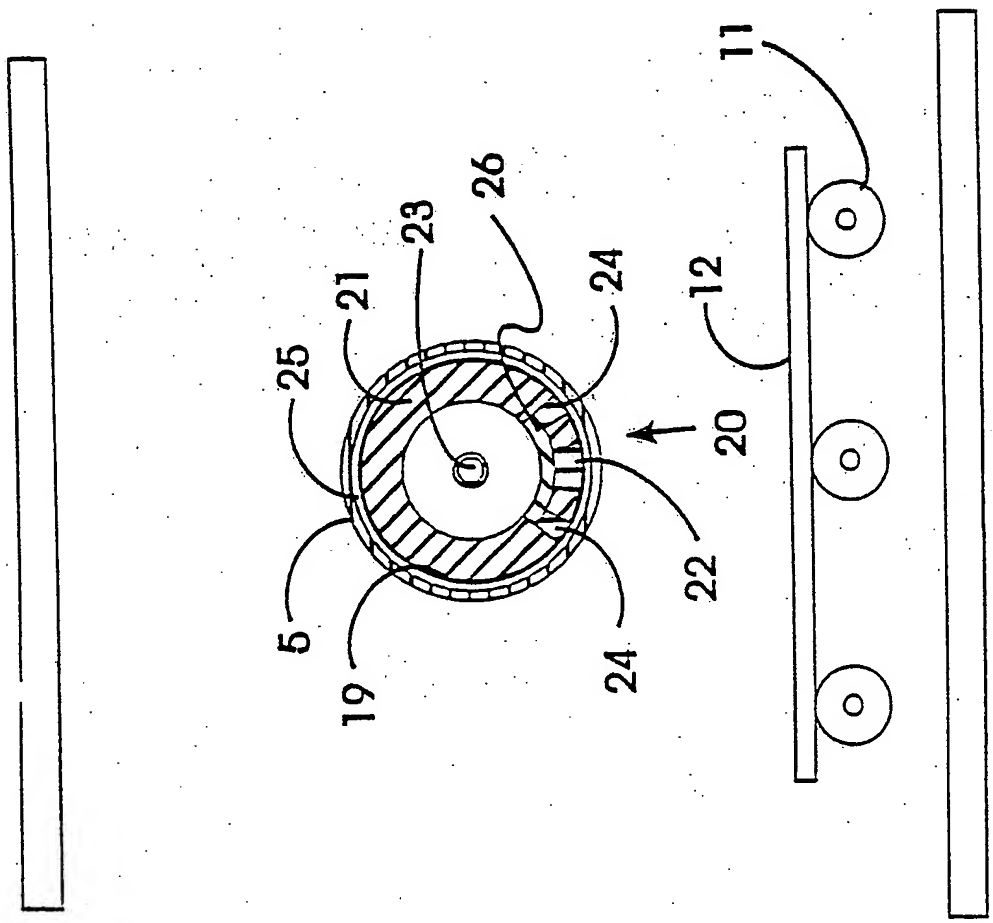



Fig. 2a

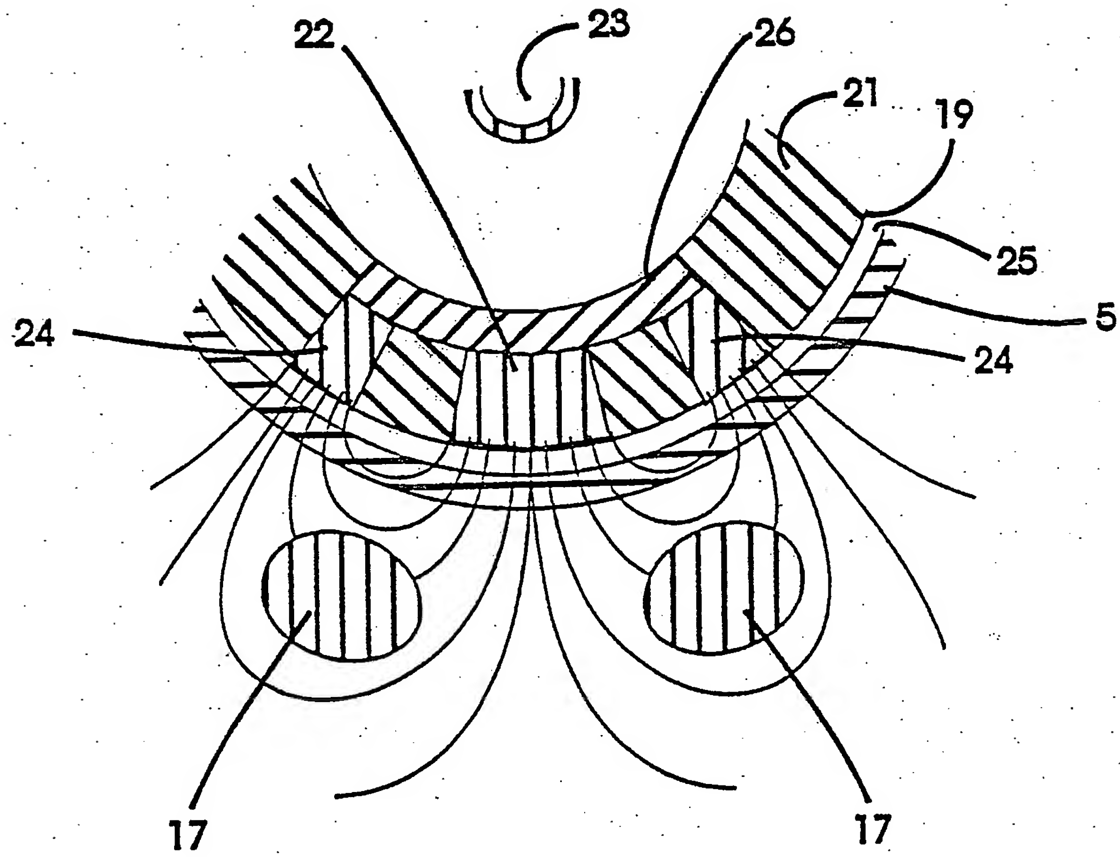



Fig. 2b

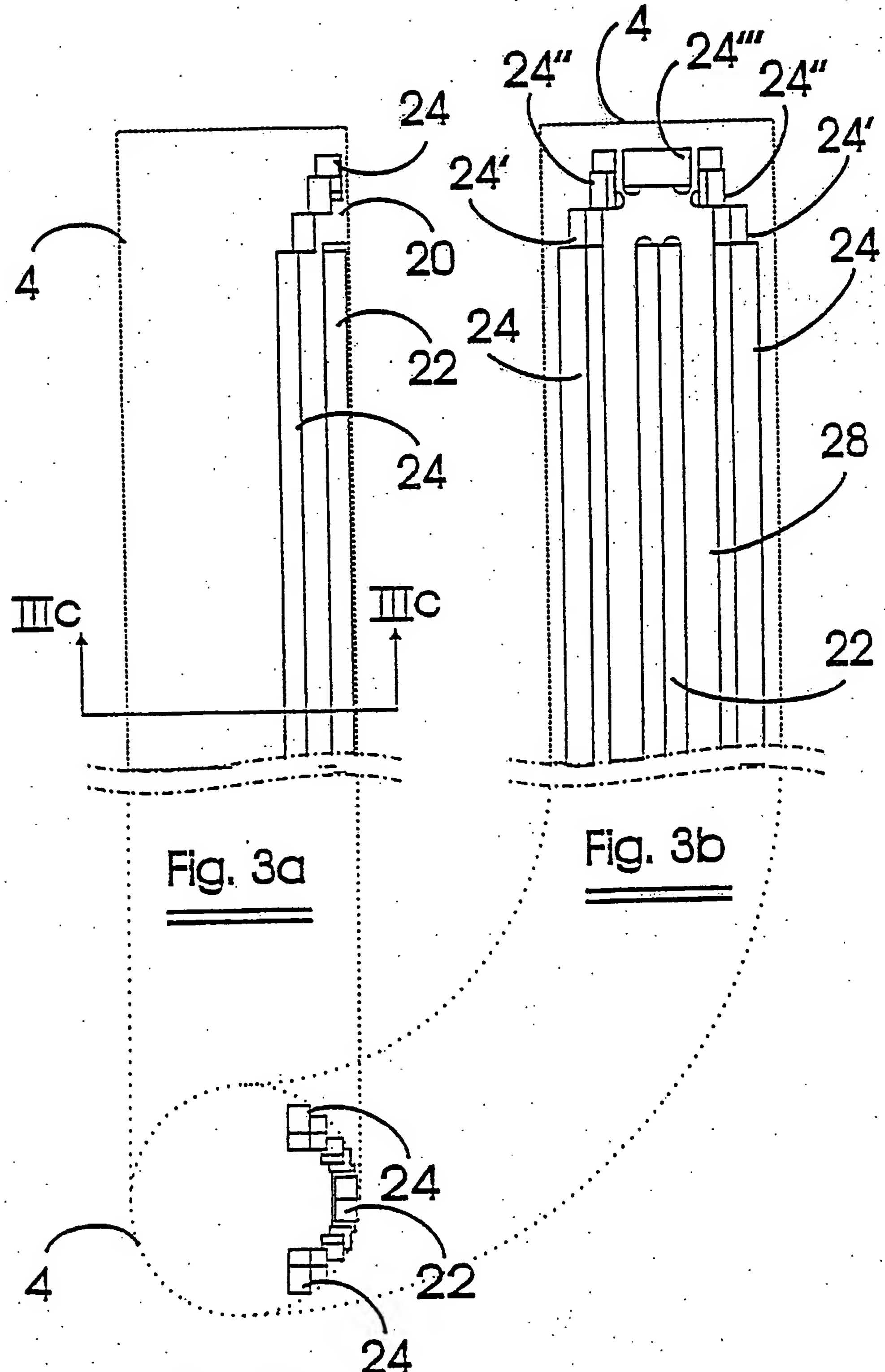



Fig. 3a

Fig. 3b

Fig. 3c

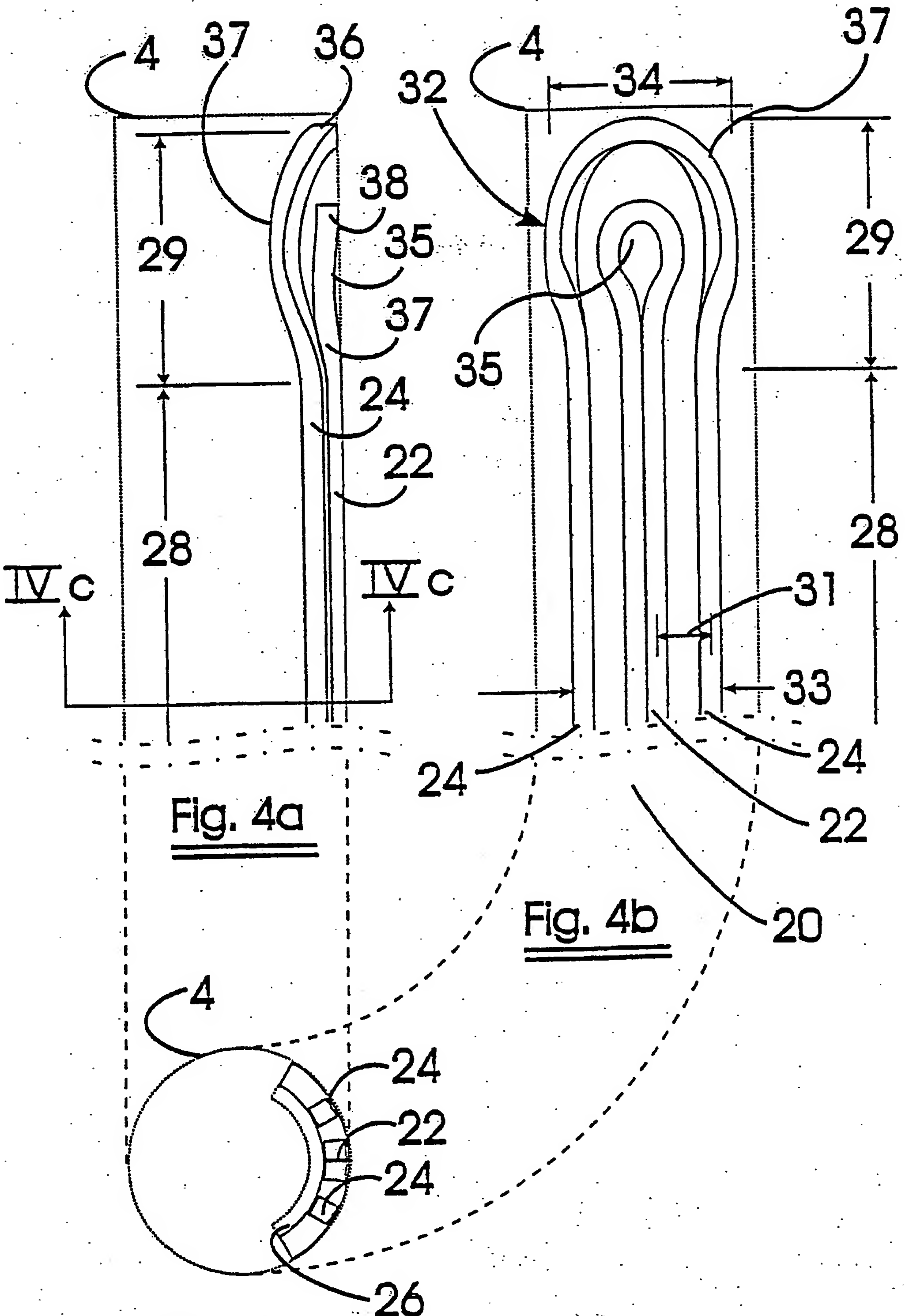



Fig. 4a

Fig. 4b

Fig. 4c

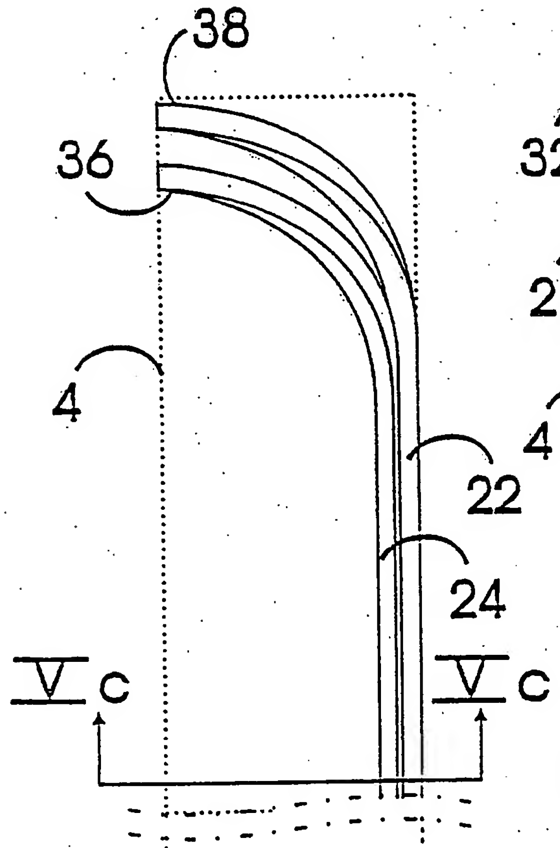



Fig. 5a

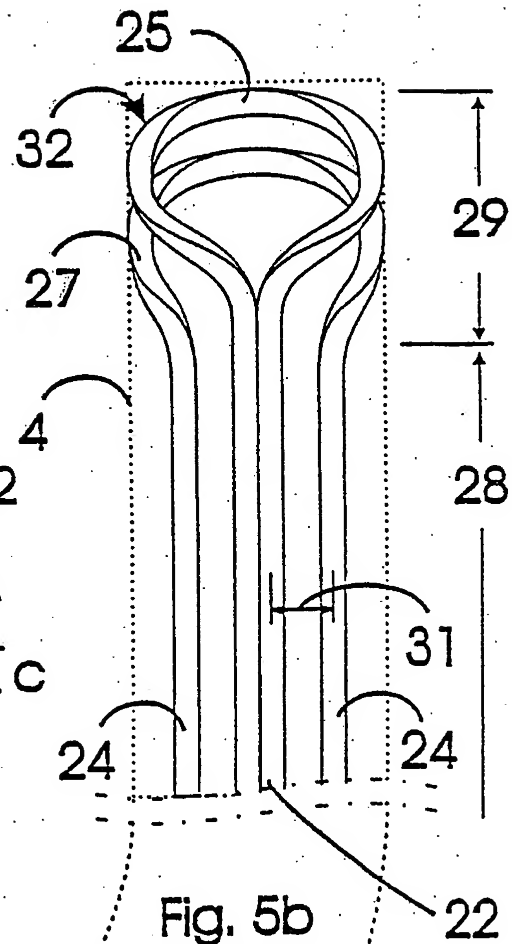



Fig. 5b

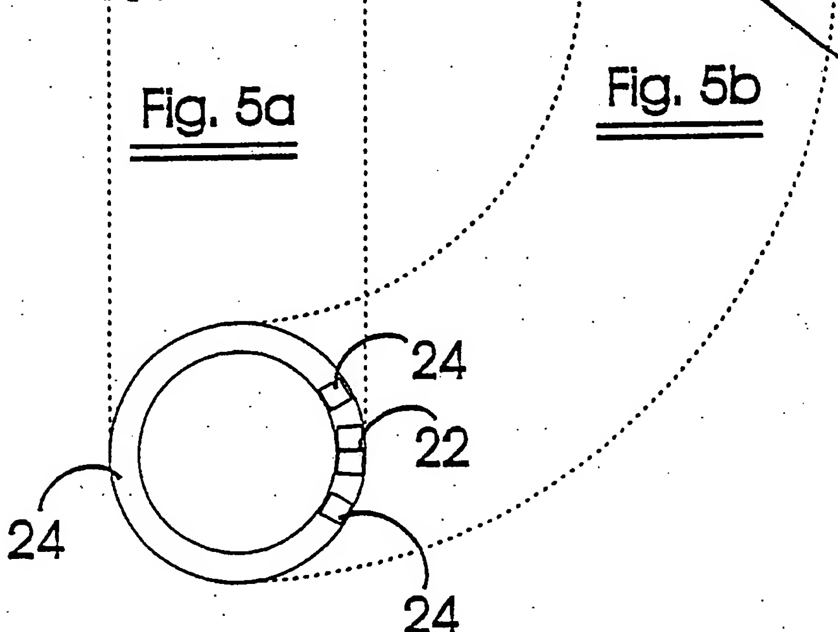



Fig. 5c

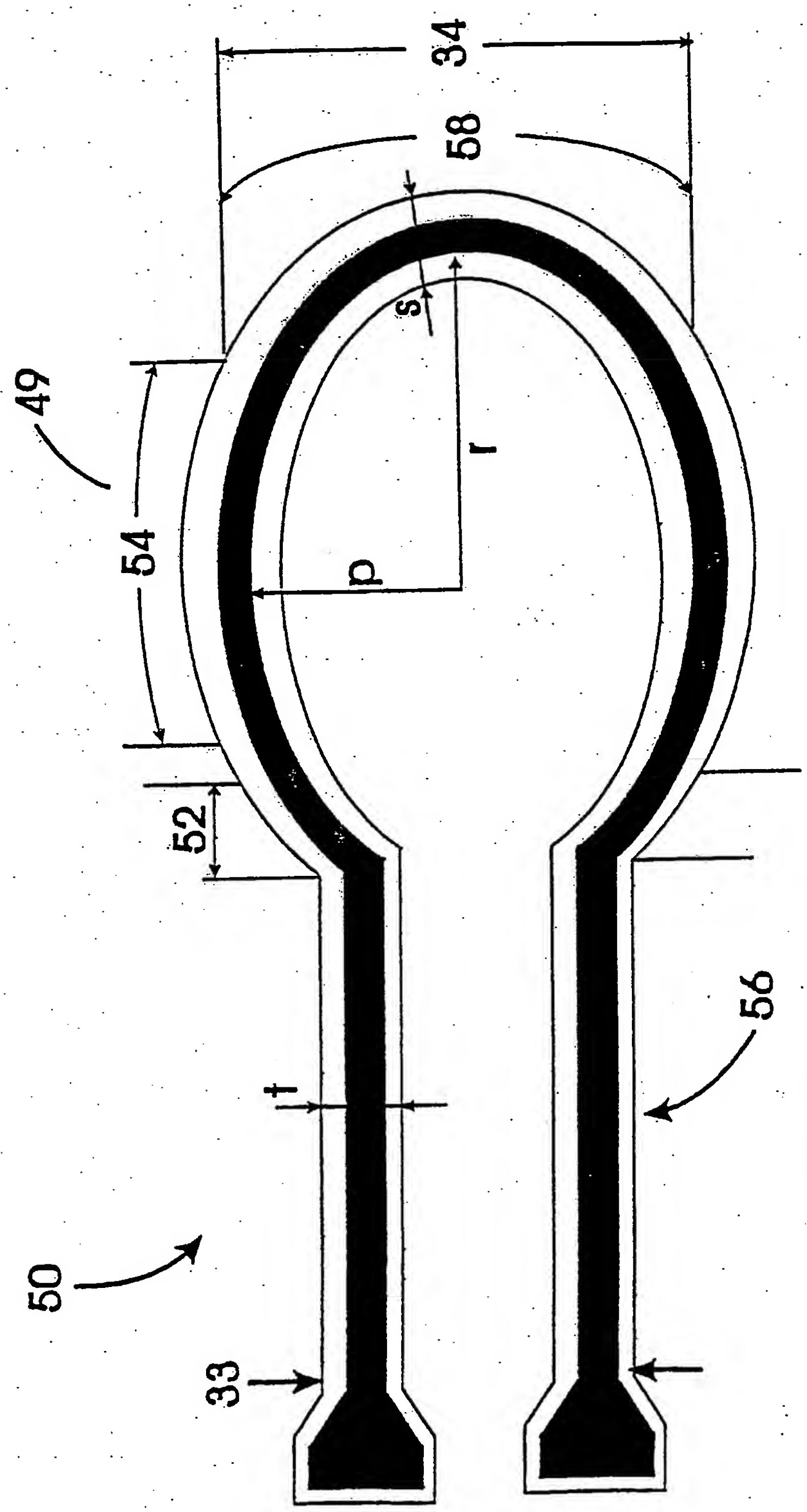
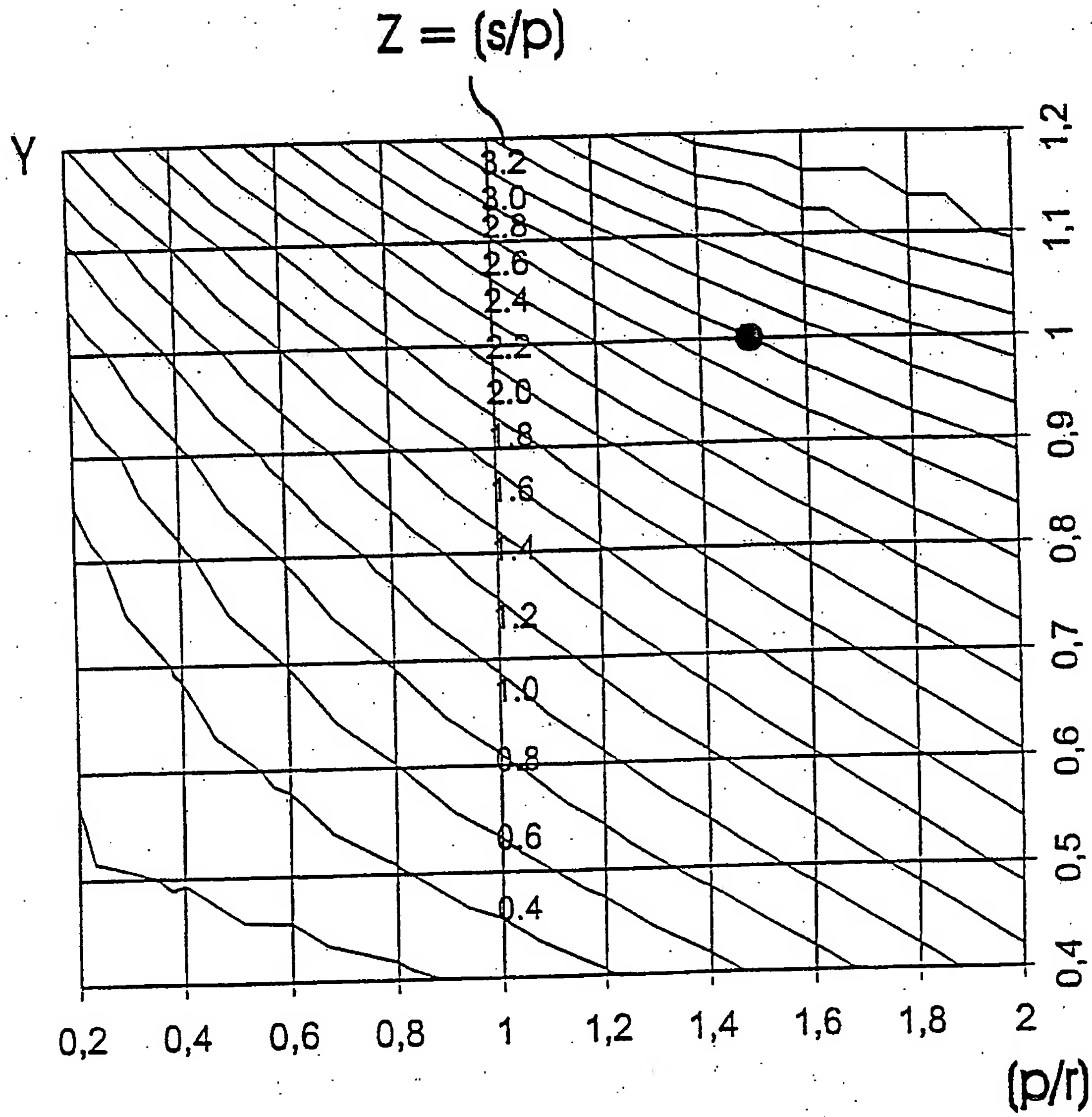



Fig. 6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0,5
0,4
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2
(p/r)

Fig. 7a

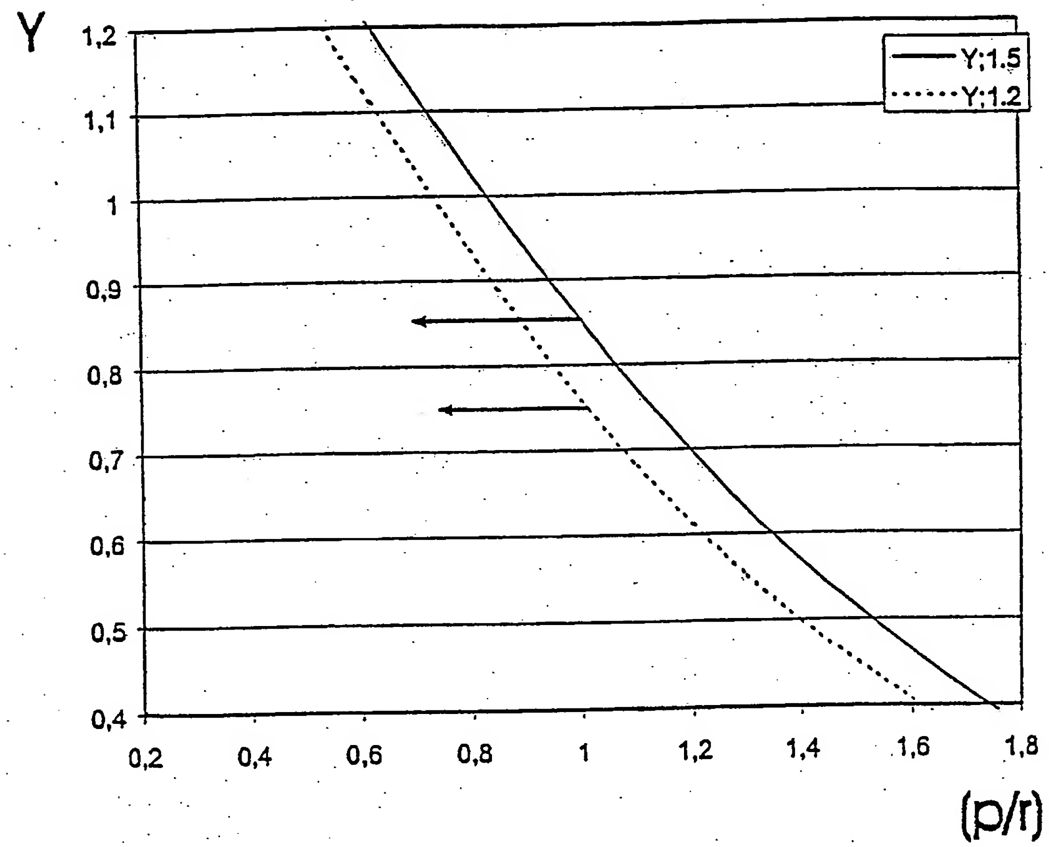


Fig. 7b

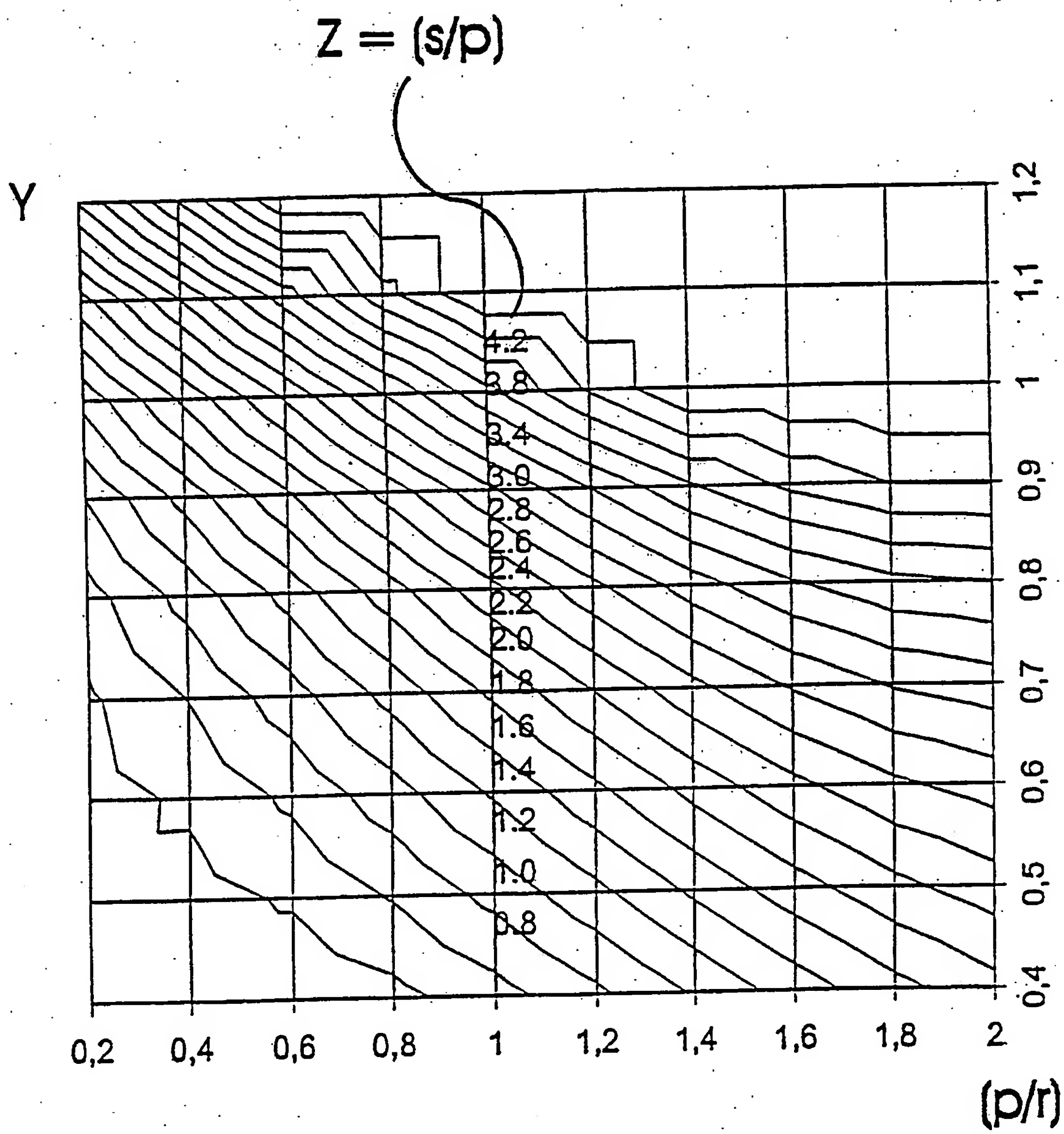
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Fig. 8a

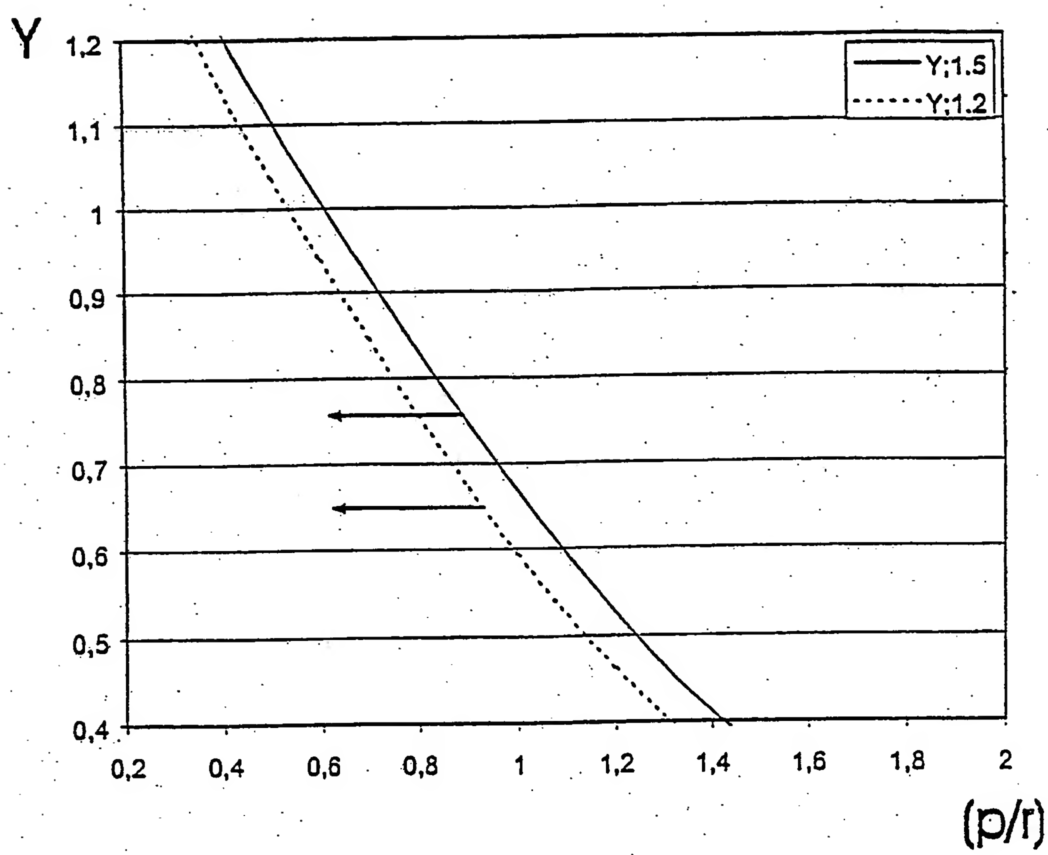


Fig. 8b

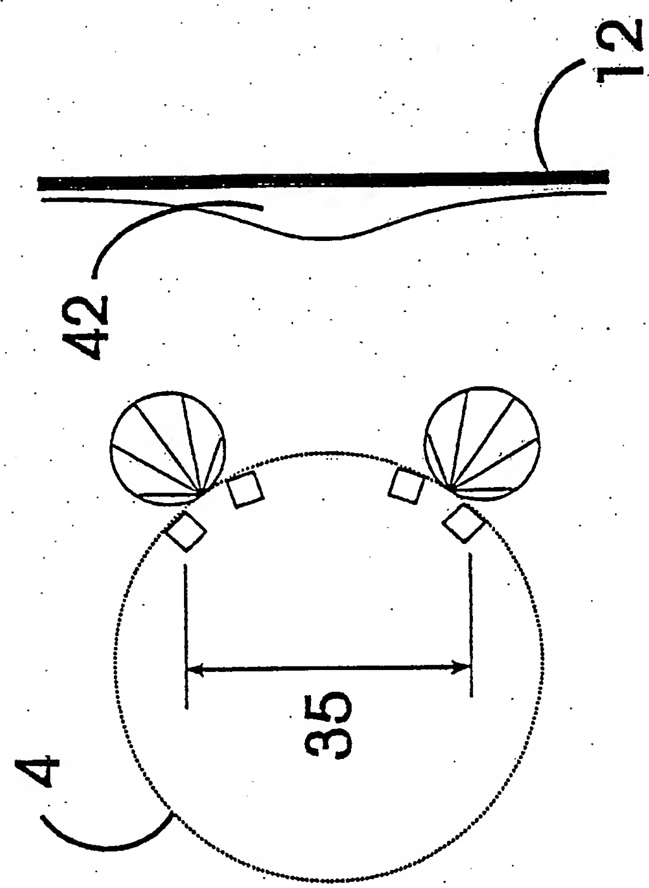


Fig. 9e

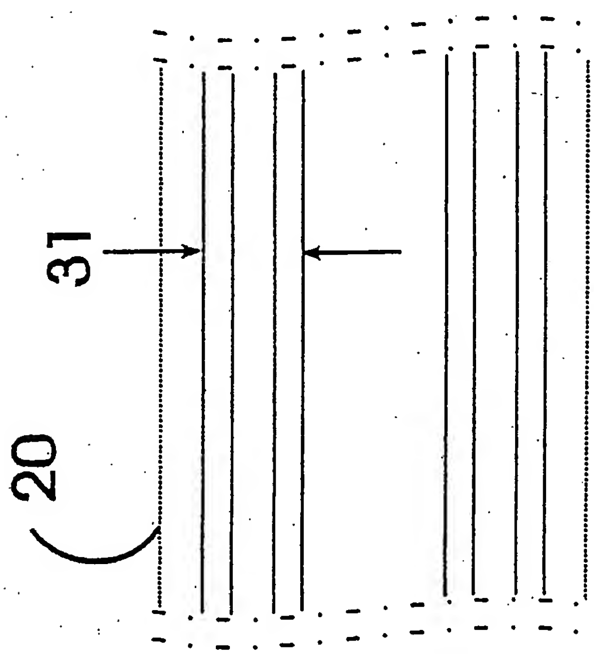


Fig. 9b

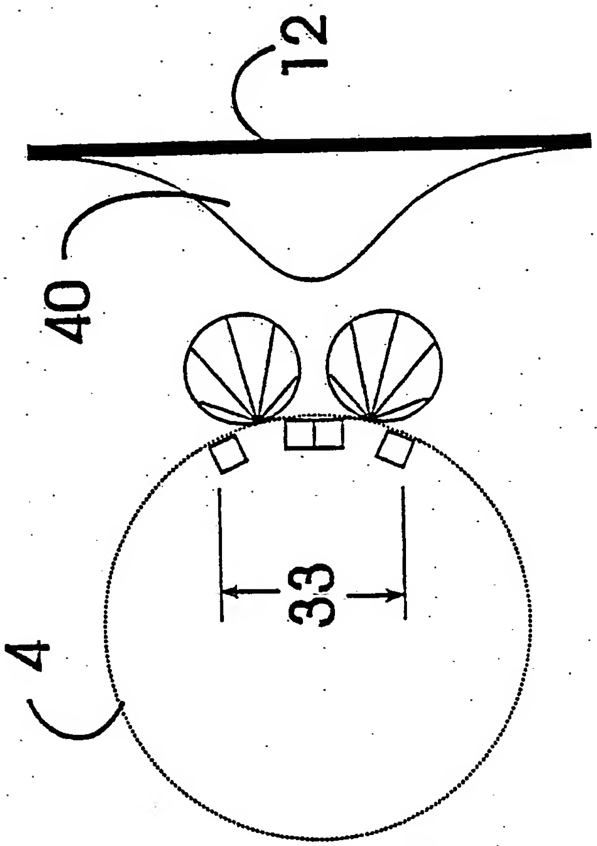


Fig. 9d

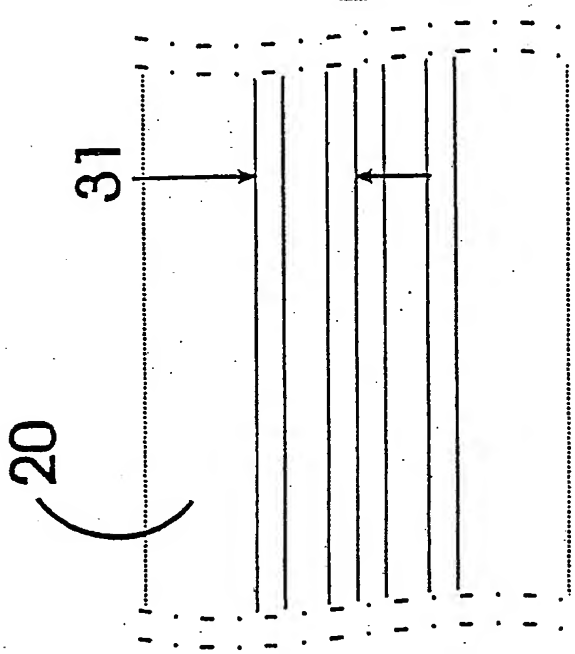


Fig. 9a

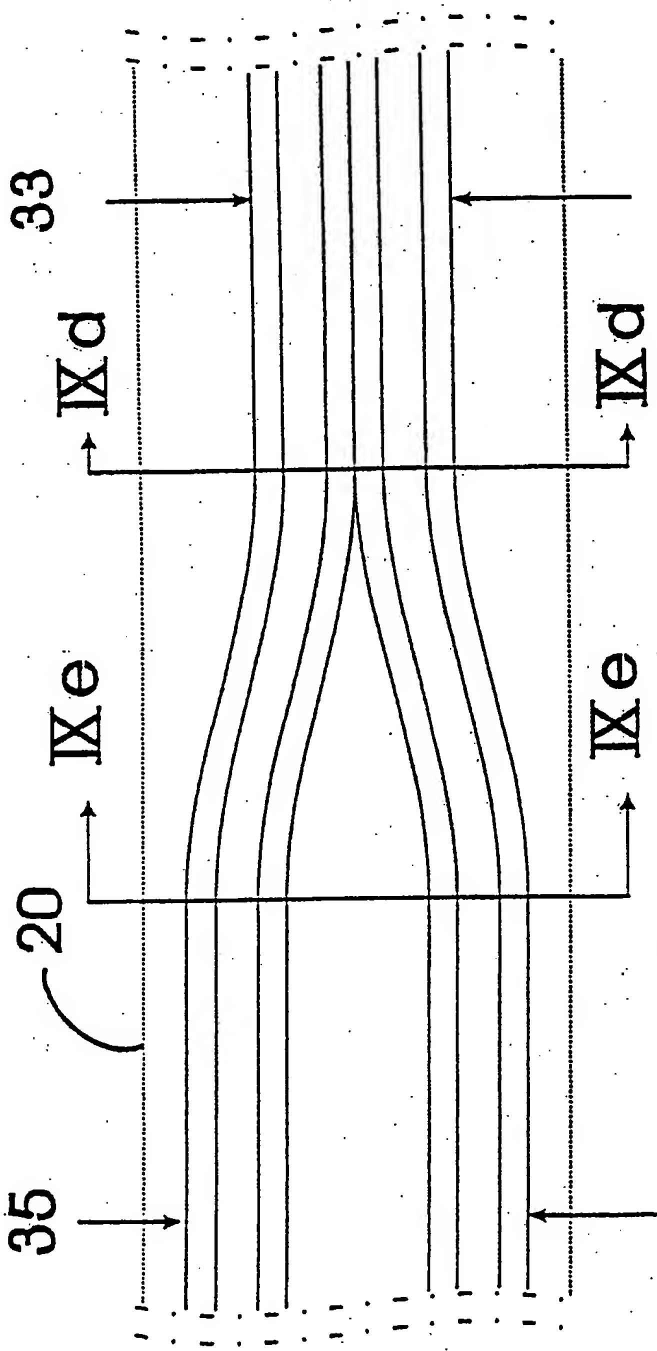


Fig. 9c

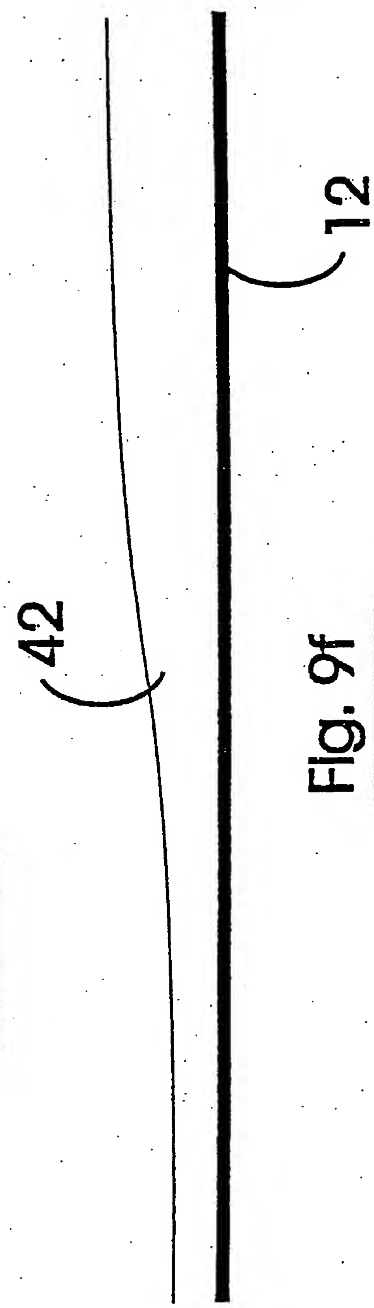


Fig. 9f

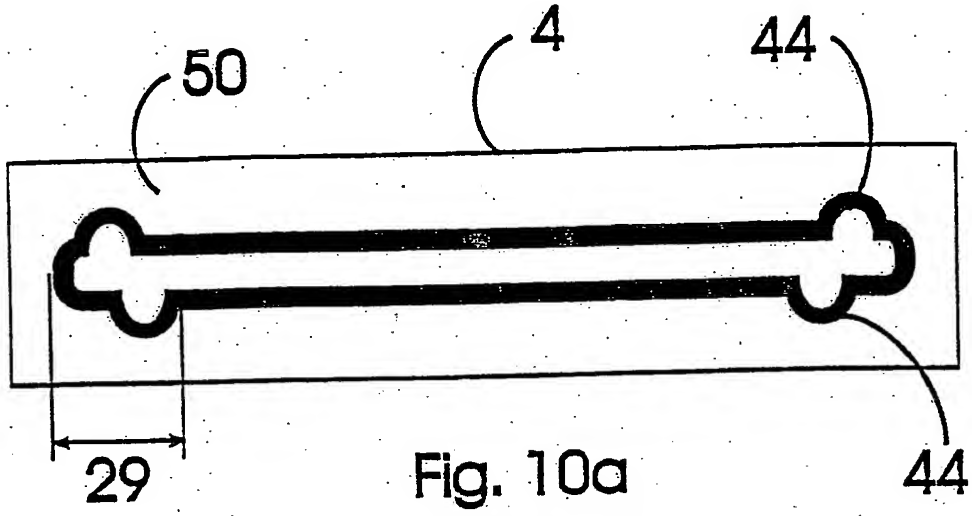


Fig. 10a

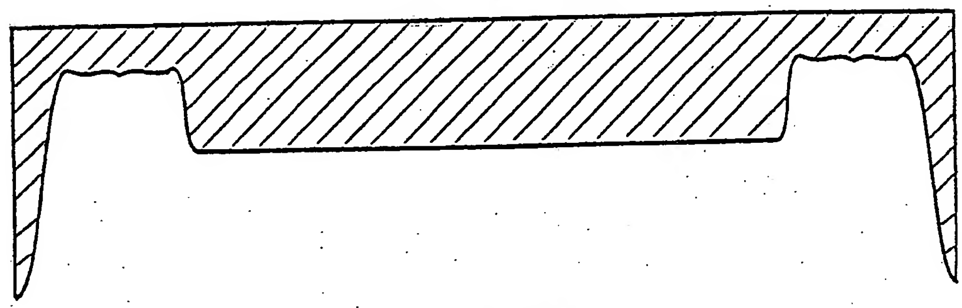

Fig. 10b

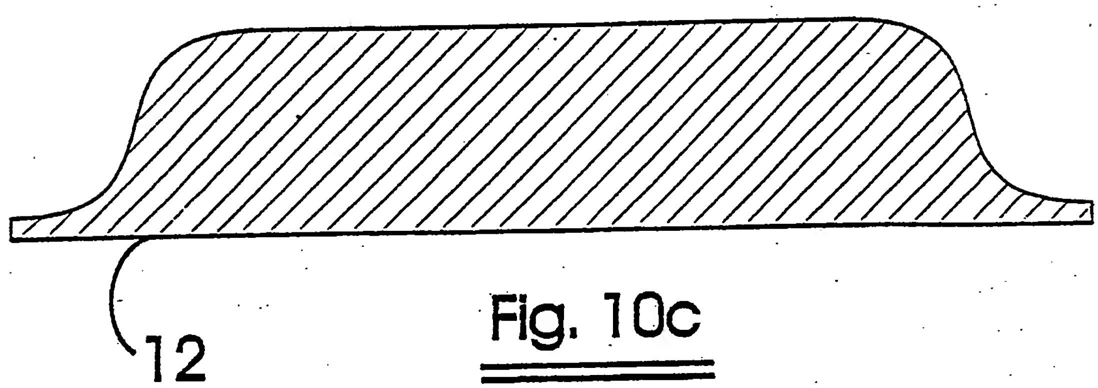


Fig. 10c

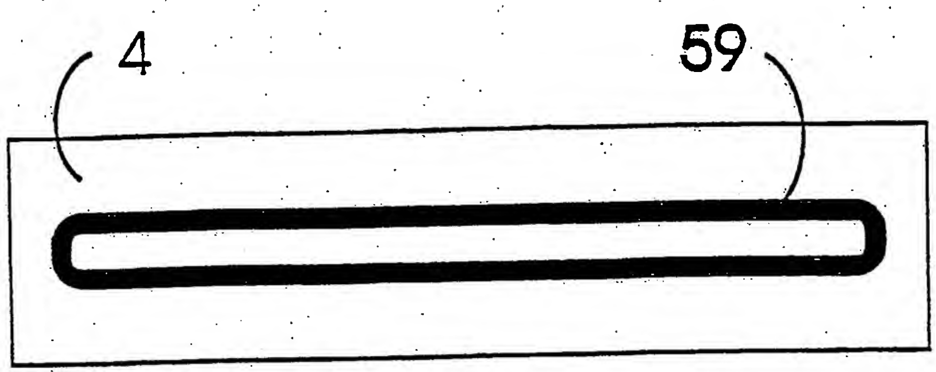


Fig. 11a

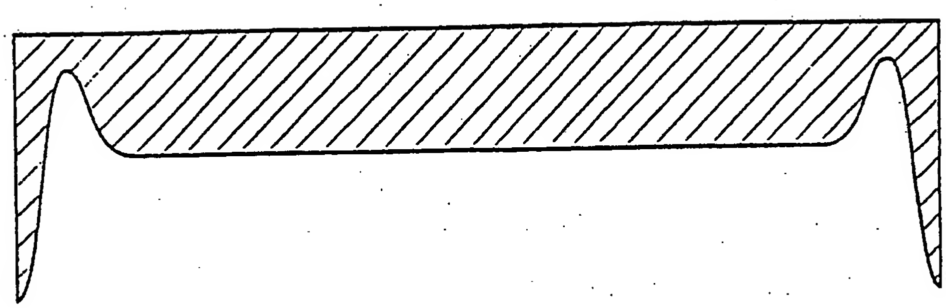

Fig. 11b

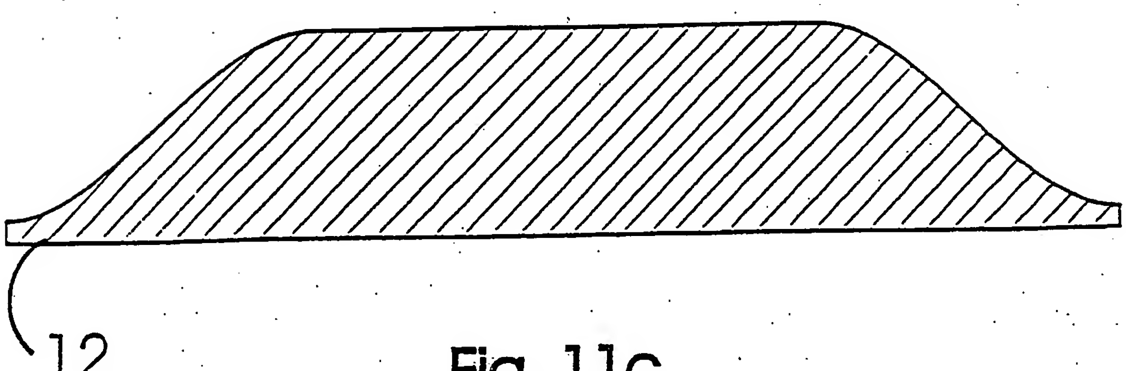


Fig. 11c

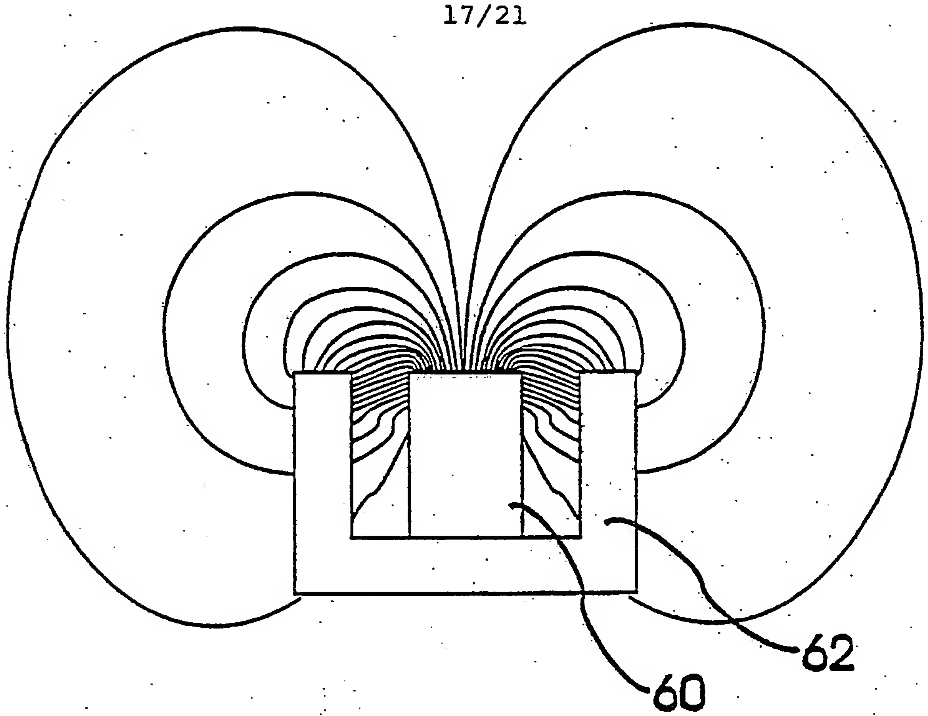


Fig. 12a

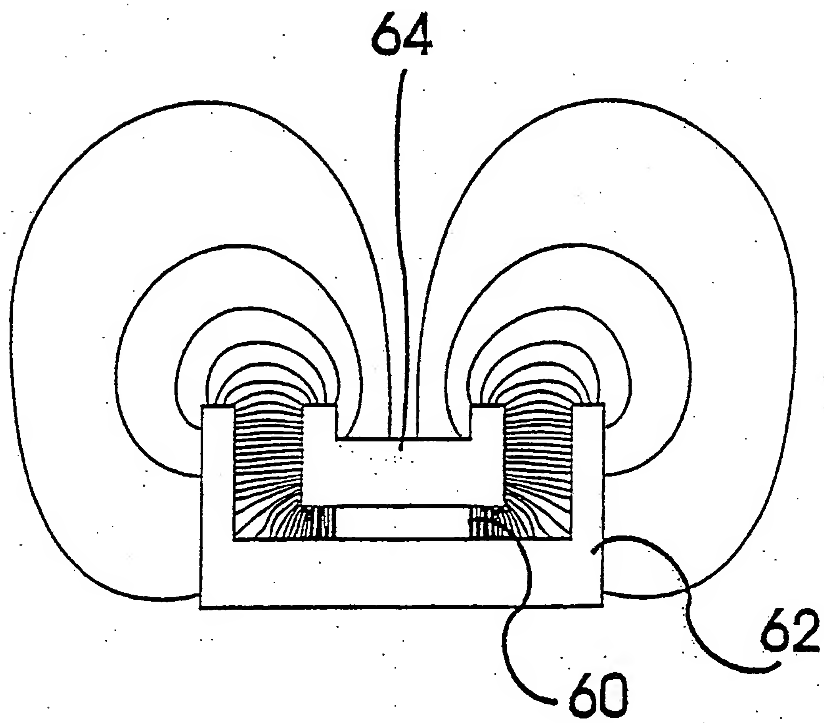


Fig. 12b

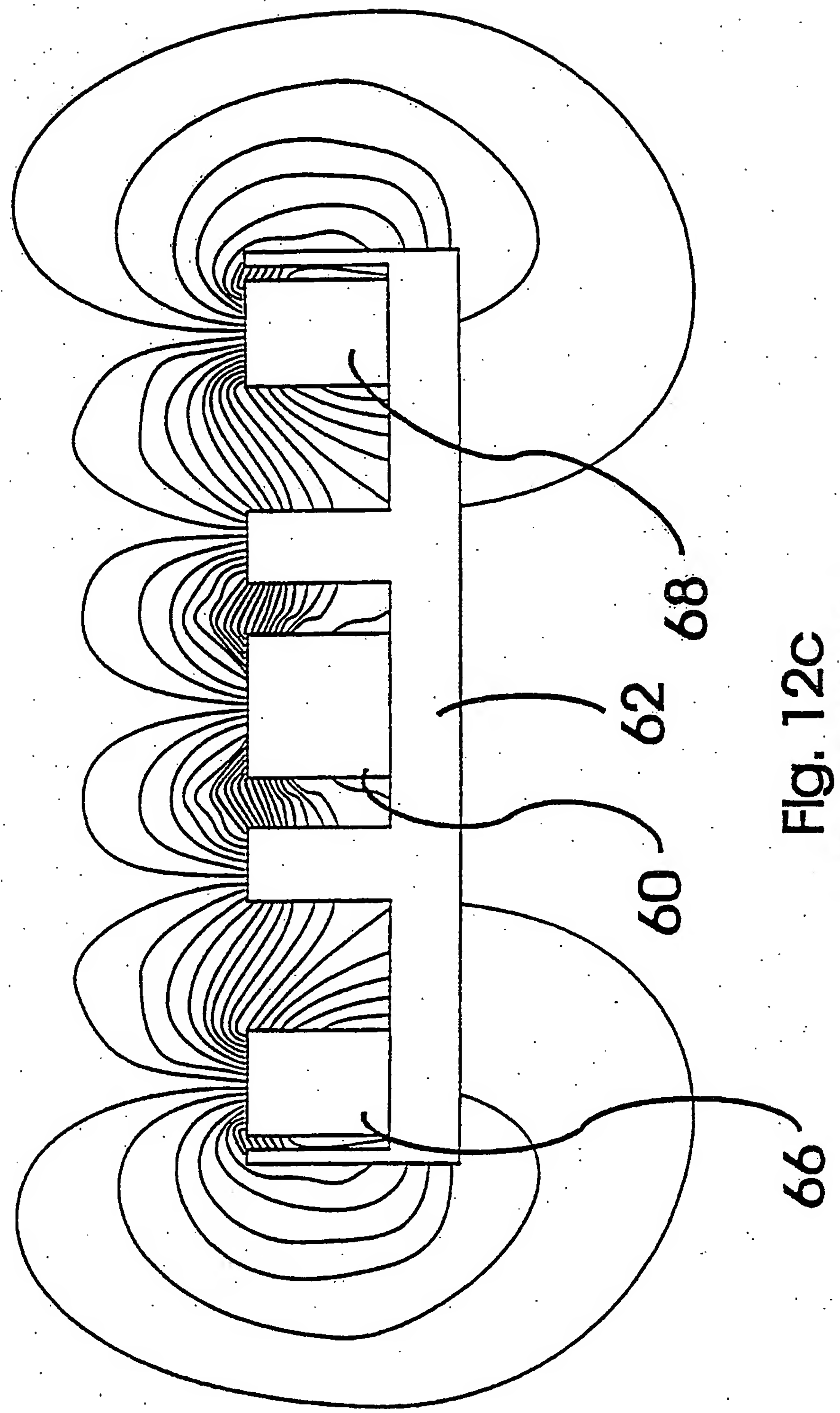


Fig. 12c

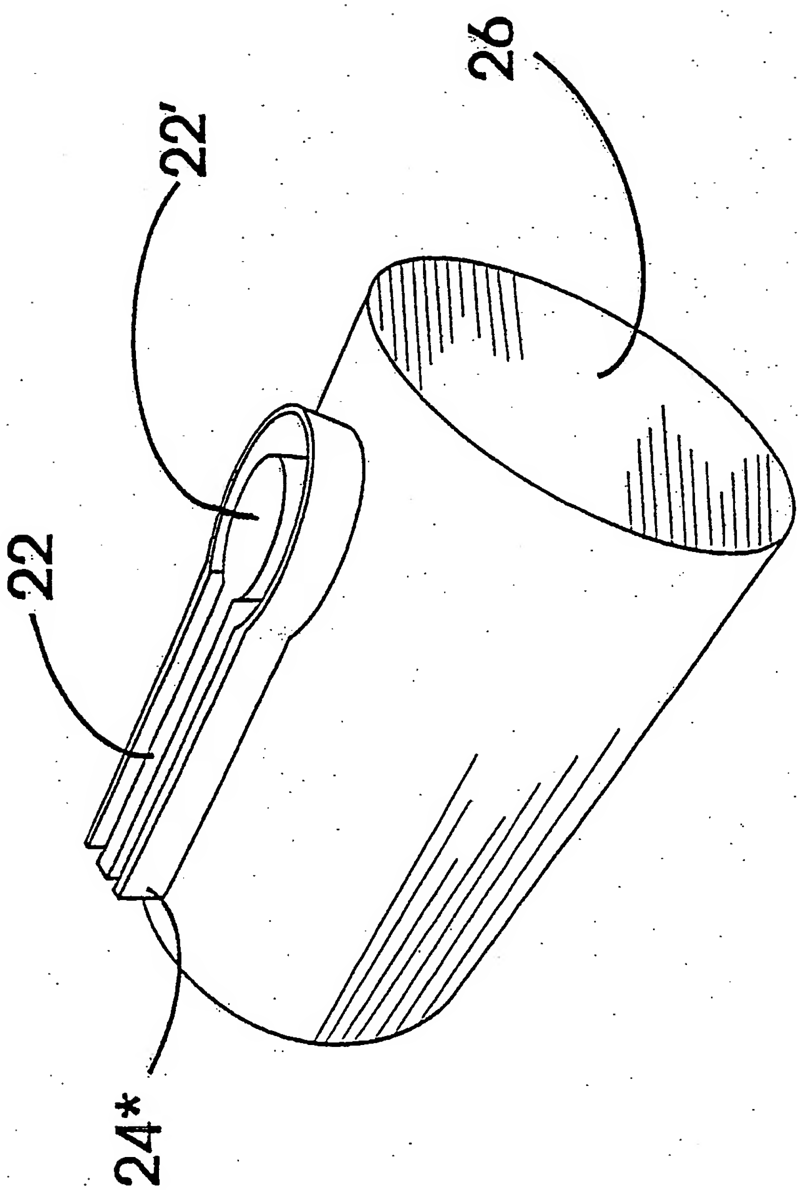


Fig. 13

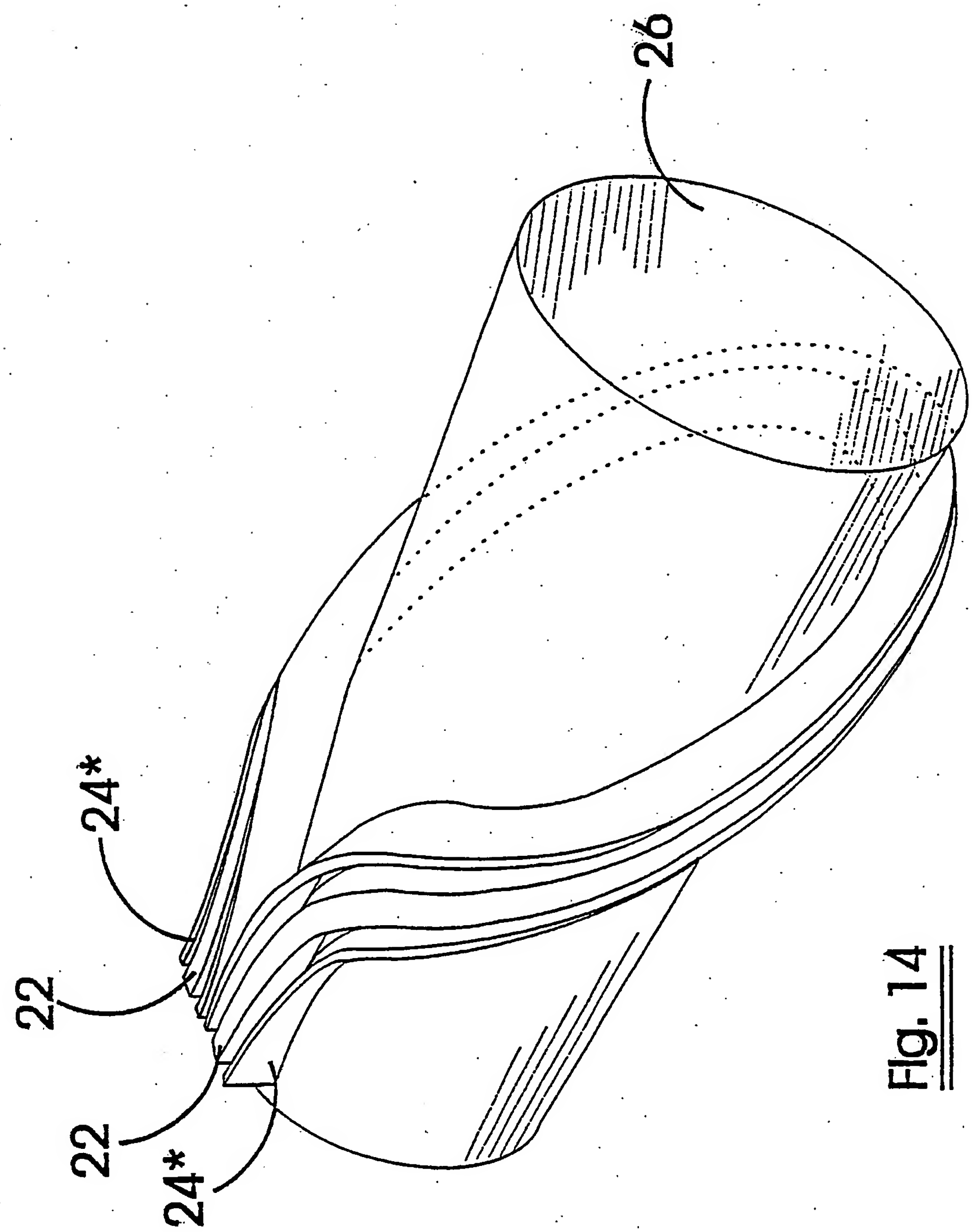


Fig. 14

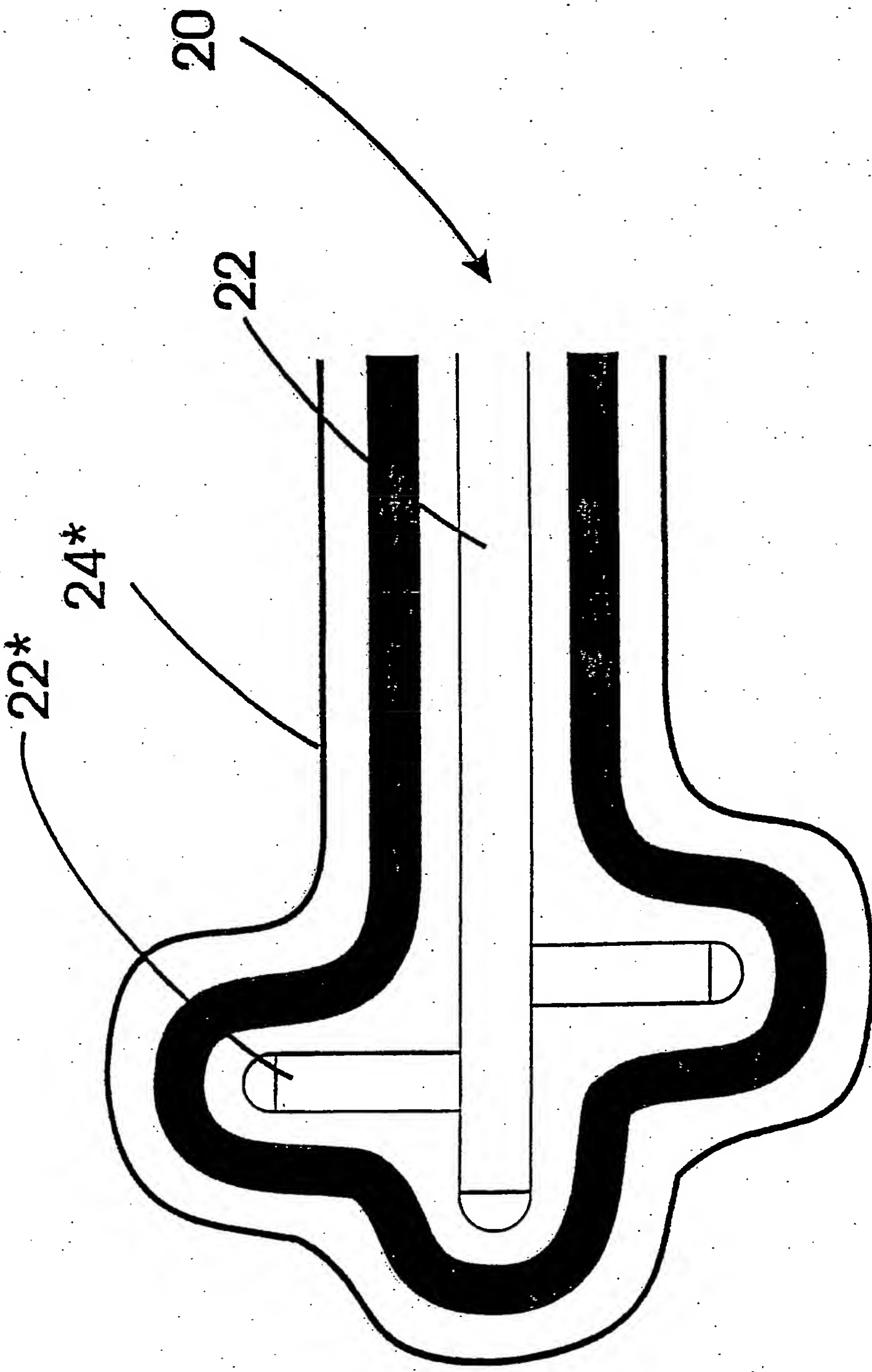


Fig. 15

# INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 99/02646

**A. CLASSIFICATION OF SUBJECT MATTER**
IPC 6 H01J37/34

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 H01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category ° | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| Y | DE 41 17 367 A (LEYBOLD AG) 3 December 1992 (1992-12-03) cited in the application column 2, line 39 - column 3, line 11; figures | 1,8,11, 12 |
| Y | DE 196 22 606 A (LEYBOLD SYSTEMS GMBH) 11 December 1997 (1997-12-11) column 1, line 38 - column 2, line 19; figures | 1,8,11, 12 |
| A | WO 96 21750 A (BOC GROUP INC ;LEHAN JOHN P (US); BYORUM HENRY (US)) 18 July 1996 (1996-07-18) cited in the application page 6, line 15 - page 11, line 11; figures 2-5 | 1,11,12 |

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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| Date of the actual completion of the international search | Date of mailing of the international search report |
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| 24 August 1999 | 31/08/1999 |

| Name and mailing address of the ISA | Authorized officer |
|---|---|
| European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016 | Schaub, G |

1

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| A | US 5 514 257 A (KOBAYASHI MASAHIKO ET AL) 7 May 1996 (1996-05-07) column 3, line 35 - column 4, line 32; figure 2 | 1,11,12 |
| A | EP 0 081 331 A (FORD MOTOR CO ;FORD WERKE AG (DE); FORD FRANCE (FR); FORD MOTOR CO) 15 June 1983 (1983-06-15) page 7, line 3 - line 16; figures | 1,11,12 |

1

# INTERNATIONAL SEARCH REPORT

Information on patent family members

Inte. ›onal Application No
PCT/EP 99/02646

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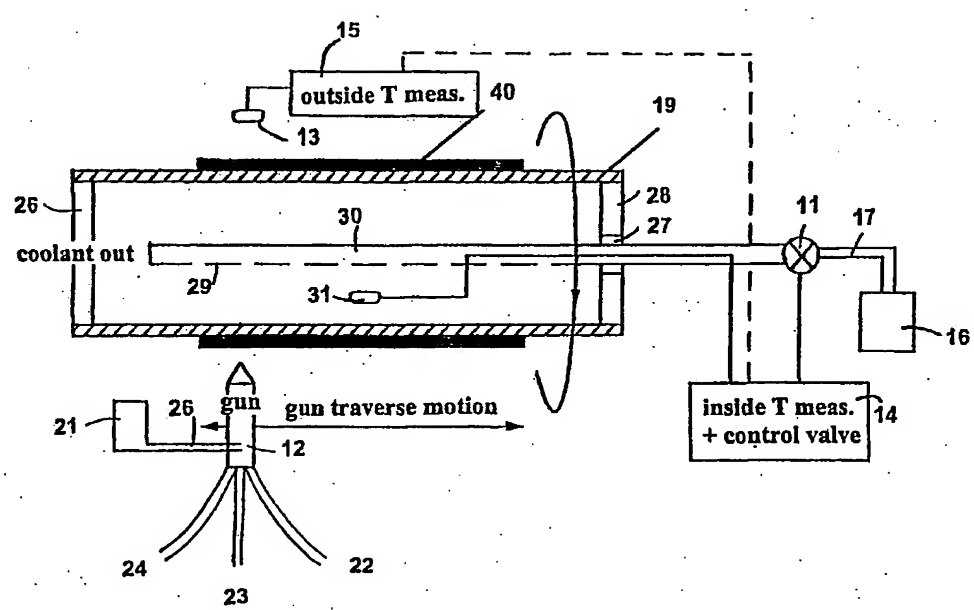


(57) Abstract

A method and an apparatus for spraying materials onto a substrate to produce a coating thereon is described which allows very thick layers of complex metal oxides to be produced. The apparatus and method are particularly suitable for producing superconducting coatings.

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# SPRAYING METHOD TO FORM A THICK COATING AND PRODUCTS OBTAINED

The present invention relates an apparatus and a method of spraying to form a coating on flat or curved substrates, for example, either as part of the direct formation of metallic or ceramic coatings such as superconductive or piezo-electric layers or for the production of targets for sputtering magnetrons having coatings which are precursors of such layers.

## TECHNICAL BACKGROUND

From EP-A-286 135 it is known to flame spray complex ceramic materials onto a substrate such as a tape to form a superconducting layer. It is suggested to pre-heat the substrate to temperatures above 540°C and to cool the coating slowly. It is further recommended to treat the coating in an atmosphere containing one of the components of the superconducting ceramic. An oxy-acetylene flame is used for the flame spraying. Thickness of up to 3 mm are described.

It is also known from US 5,196,400 to plasma spray a coating onto a target for use in a sputtering magnetron to sputter a Y-Ba-CuO superconductor coating. Deposition of only a thin target coating of 0.5 mm is reported.

The production of superconducting powders using flame spraying is reported in US 5,140,005. An oxy-acetylene flame is used. It is tacitly accepted that the high temperature of the flame changes the stoichiometric ratios of the components and that this has to be compensated by increasing the more volatile components in the original mixtures. US 5,045,365 describes a method of cooling a oxy-acetylene flame-sprayed substrate with water. Without special precautions, water cooling is unsuitable for superconductors due to the water vapour produced.

EP-A-355 736 describes production of flat targets with metal oxides up to a layer thickness of 3 mm. WO 98/0833 describes the production of < 20 micron thick layers of superconducting metal oxide mixtures.

The article by Murakami et. al. "Rapidly Solidified Thick Deposit Layers of Fe-C-Mo Alloys by Flame Spraying" describes up to 1.5 mm thick rapidly

cooled thick layers of Fe-C-Mo alloys by flame spraying. Special precautions were taken to produce dense layers, e.g. direct application of cryogenic gas on the coating during application.

EP-A-586 809 describes the metal spraying application of a layer of relatively homogeneous material (nickel coated silicon) which is much easier to handle than the heterogeneous oxide mixtures contemplated by the present invention. Layer thicknesses of up to 8 mm are described but 3 to 5 mm is preferred. Various layers are proposed including a Ni-Al layer for improving adhesion between the deposited layer and the substrate. A Ni-Al adhesion promoter is known from DE-A-33 18 828.

Plasma spraying of superconducting materials is described in EP-A-288711 up to a thickness of 250 micron.

It is an object of the present invention to provide an apparatus and a method of spraying heterogeneous metal oxides to form a ceramic coating on flat or curved substrates.

It is a further object of the present invention to provide an apparatus and a method of spraying heterogeneous metal oxides to form a thick walled ceramic coating on flat or curved substrates which is structurally sound.

It is a further object of the present invention to provide an apparatus and a method of spraying to form a thick walled coating of a superconducting ceramic material.

It is still a further object of the present invention to provide an apparatus and a method of spraying suitable for forming a thick walled ceramic coating on flat or curved targets to be used in a sputtering magnetron.

It is still another object of the present invention to provide a method of producing a (magnetron) vacuum sputtering target as well as the target itself with improved thermal and electrical conductivity and high mechanical strength using a spraying process employing dedicated powder formulations.

## SUMMARY OF THE INVENTION

One aspect of the present invention is to provide a substrate with a coating of a combination of metal oxides having a thickness greater than 3 mm more preferably greater than 5 mm and most preferably greater than 8 mm. Preferably, the coating is deposited by spraying, e.g. flame or plasma spraying. Preferably, the substrate is cylindrical and is more preferably is suitable as a cylindrical target substrate for a sputtering magnetron. The combination of oxides preferably comprises at least a superconductive precursor or a superconductor. The thermal conductivity of the deposited material is preferably between 1 and 5 $Wm^{-1}K^{-1}$. When deposited on a steel substrate the thermal conductivity of the composite preferably lies within the range 25 to 125 $Wm^{-1}K^{-1}$. These values are particularly preferred for $YBa_2Cu_3O_7$ coatings. Preferably, an adhesion promoter layer is applied onto the substrate before application of the coating of the metal oxide combination. The adhesion promoter may be a layer of Ni-Al or a layer of an In-alloy, for example. The deposited coating is preferably impact resistant, e.g. withstands impact of a 0.036 kg steel ball from a height of 2 metres. Preferably, about 20% or up to 30% of a noble metal is included in the oxide material to improve electrical and thermal properties of the deposited layer. The noble metal is preferably silver. The noble metal may in included as a salt or oxide, e.g. silver nitrate or silver oxide, in the material to be sprayed. Preferably, the electrical resistivity of the deposited layer is lower than $15 \times 10^{-6}$ Ohm.m, more preferably lower than $10 \times 10^{-6}$ and most preferably less than $5 \times 10^{-6}$ Ohm.m. Values below $1 \times 10^{-6}$ Ohm.m can be achieved. Up to 30% of a noble metal such as silver may be added to lower the resistivity. These values are particularly preferred for $YBa_2Cu_3O_7$ coatings.

The electrical , thermal and mechanical properties of the coating deposited in accordance with the present invention should be sufficient that the deposited layer can be applied to a suitable substrate by means of a sputtering magnetron preferably at a static sputtering deposition speed of at least 5 nm/minute, more preferably, at 20 nm/minute and most preferably at at least 40 nm/minute.

When a superconductor precursor or a superconductive material is

deposited, at least 10% of the coating is in the superconducting phase, more preferably 15%. This may be assisted by a subsequent limited thermal treatment, e.g. 3 hours and 940°C, after deposition.

The present invention also includes a method of depositing by spraying a superconductor precursor layer onto a cylindrical target for a sputtering magnetron, the layer having a thickness of at least 3 mm, and at least 10% of the layer being in a superconductive phase. The present invention also includes a method of depositing by spraying a layer onto a substrate, the layer having a thickness of at least 5 mm, and the coating comprising metal oxides.

In accordance with one aspect of the present invention a flame spraying apparatus is provided for depositing a metal oxide combination onto a substrate to produce a coating thereon, comprising: a burner for producing a flame; an inlet for feeding material to be sprayed through the flame, the flame imparting a temperature to the material to be sprayed of 1500°C or less, preferably 1200°C or less. Preferably the temperature imparted may be a little higher than the melting point of the powder to be sprayed, e.g. 600 to 1000°C for some metal oxides. Preferably, the thickness of the deposited coating is greater than 3 mm more preferably greater than 5 mm and most preferably greater than 8 mm.

Another aspect of the present invention is to provide a flame spraying apparatus for depositing a metal oxide combination onto a substrate to produce a coating thereon, comprising: a flame spraying gun; and a cooling system for the substrate, the cooling system including a device for bringing a cryogenic fluid into contact with the substrate. Preferably, the thickness of the deposited coating is greater than 3 mm more preferably greater than 5 mm and most preferably greater than 8 mm. The input material for the sprayer may be a liquid solution of soluble compounds (e.g. nitrates) which decompose thermally into ceramic component oxides, liquid slurries of the ceramic components or metal powders, or dry metal or ceramic powders or precursors of the ceramic components, e.g. nitrates, of such powders.

The present invention may provide a method of flame spraying a

combination of metal oxide materials onto a substrate to produce a coating thereon, comprising: generating a flame; feeding the material to be sprayed through the flame, the flame imparting a temperature to the material to be sprayed of 1500°C or less, preferably 1200°C or less. Preferably the temperature imparted may be a little higher than the melting point of the powder to be sprayed, e.g. 600 to 1000°C for some metal oxides.

The present invention may also provide a method of flame spraying metal oxide combinations onto a substrate to produce a coating thereon, comprising: generating a flame for spraying the materials; and cooling the substrate by bringing a cryogenic fluid into contact with the substrate.

The present invention may also provide a method of flame spraying a superconducting ceramic material or a precursor thereof onto a substrate to produce a coating thereon, comprising: generating a flame for spraying the ceramic material; depositing the coating on the substrate; and during deposition of the coating, cooling the substrate so that the solidified coating thereon has a temperature between room temperature (~25°C) and 150°C, preferably room temperature (~25°C) and 100°C. Water or cryogenic fluid cooling are particularly preferred.

One linking concept between the above methods and apparatus is control of the total heat energy into the spraying/coating system. This can be achieved by careful control of parameters which influence the energy input such as spraying distance, spray head traverse speed, rotation speed of a cylindrical substrate, powder dwell time in the hot exit plume from the spray head, particle velocity exiting the spray head, cooling method and rate of cooling the substrate during coating deposition.

The present invention also includes a method of reconditioning a target for a sputtering magnetron by flame spraying or atmospheric plasma spraying as well as a reconditioned target as made in accordance with the method. The target material or coating is preferably a ceramic coating, in particular a superconducting or superconductor precursor coating.

The final coating is preferably a metallic or ceramic layer, in particular a superconducting or piezo-electric layer or a precursor thereof. The present invention includes a method of spray drying a liquid to form a powder suitable for flame spraying. The spray dried powder may be sintered. The present invention also includes a manufacturing method for depositing a coating on a substrate comprising the steps of: spray drying a precursor liquid to form a powder and flame spraying the powder to form a coating on a substrate. The substrate may be a target for a sputtering magnetron and the final coating may sputtered onto a final substrate in the sputtering magnetron. The ceramic powder may be sintered after the spray drying step. The flame of the flame spray gun preferably imparts a temperature to the powder to be sprayed of 1500°C or less, preferably 1200°C or less. Preferably the temperature imparted may be a little higher than the melting point of the powder to be sprayed, e.g. 600 to 1000°C for some metal oxides. During flame spraying the target is preferably cooled by bringing a cryogenic fluid into contact with the target. In particular the cooling device should maintain the solidified coating at a temperature between room temperature (~25°C) and 150°C, more preferably between room temperature (~25°C) and 100 °C.

The present invention includes an apparatus for spray drying a liquid to form a powder suitable for flame spraying. The present invention may also include an apparatus for depositing a coating on a substrate comprising: a spray drier for drying a precursor liquid to a powder, and a flame sprayer for flame spraying the powder to form a coating on a substrate. The substrate may be a target for a magnetron. Additionally, a sputtering magnetron for sputtering the final coating onto the final substrate using the target may be provided. The flame of the flame spray gun preferably imparts a temperature to the powder to be sprayed of slightly above the melting point of the sprayed material. Preferably the temperature imparted is 1500°C or less, preferably 1200°C or less. Temperatures of 600 to 850 °C may be suitable for some metal oxides. In the flame sprayer a cooling system for the target is preferably provided, the cooling system including a device for bringing a cryogenic fluid into contact with the target. In particular

the cooling device should maintain the solidified coating at a temperature between room temperature (~25°C) and 150°C, more preferably between room temperature (~25°C) and 100 °C.

The above methods may be used, for example, either as part of the direct formation of superconductive or piezo-electric layers on the substrate, e.g. a tape, or for the production of coatings on targets for use in a sputtering magnetron to sputter a superconducting layer onto a final substrate. The present invention may provide oxide sputtering targets supporting very high power dissipation thus enabling high sputter deposition rates of at least 50 nm/min.

The dependent claims describe additional individual embodiments of the present invention. The present invention will now be described with reference to the following drawings.

## BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic representation of a flame spraying apparatus in accordance with one embodiment of the present invention.

Fig. 2 is a schematic representation of a flame spraying apparatus in accordance with another embodiment of the present invention.

Fig. 3 is a schematic representation of a spray drying apparatus in accordance with another embodiment of the present invention.

## DESCRIPTION OF THE ILLUSTRATIVE EMBODIMENTS

The present invention will be described with reference to certain specific embodiments and with reference to certain specific drawings but the invention is not limited thereto but only by the claims. In particular, the present invention will mainly be described with reference to the deposition of a superconductor precursor or superconductive coatings but the invention is not limited thereto but may be used advantageously with other heterogeneous coatings such as ceramic coatings, particularly those having special properties such as piezo-electric coatings and in particular coatings which contain components which can be

degraded by high temperatures or which are more volatile than other components. More particularly the present invention will be described with reference to the manufacture of $YBa_2Cu_3O_7$ superconducting powders and coatings but the invention is not limited thereto but only by the claims. Further one way of carrying out the present invention will be described with reference to low temperature flame spraying but the present invention is not limited thereto. By carrying out the invention in accordance with the processing details and principles described below thick layer (greater than 3 mm, more preferably greater than 5 mm and most preferably greater than 8 mm) metal oxide combination coatings suitable for use as a sputtering magnetron target have been applied by oxy-acetylene flame spraying with water cooling or by atmospheric pressure or low-pressure plasma spraying to substrates including cylindrical substrates used in rotating cathode magnetrons. During plasma spraying gasses may be used such as argon or mixtures of argon and other gasses to shield the plasma spray. Also the present invention will mainly be described with reference to an input to the flame spraying head of spray dried powder. The present invention is not limited thereto but includes other forms of input materials such as a mixture of the metal oxides, including slurries thereof or mixtures of precursors of metal oxides such as metal nitrates as well as slurries and solutions thereof.

Fig. 1 is a schematic diagram of the flame spraying apparatus 10 in accordance with a first embodiment of the present invention. A flame spraying gun is represented schematically at 12. The gun 12 may be a commercially available flame spraying gun as for instance available from Sulzer Metco, Westbury, NY, USA or a high velocity oxy-fuel spraying gun available from the same company. The gun 12 may be provided with an air pincher. The gun 12 may be fed with fuel gas in pipe 22, oxygen in pipe 23 and gun cooling air in pipe 24. Additional gases may be supplied to the gun 12 as described for instance in US 5,273,957 or EP-A-413 296. Material to be coated is fed in powder or liquid form, e.g. a dry powder, a slurry of the powder and a liquid or in solution, to the gun via conduit 26 from hopper 21. Gun 12 is mounted on a drive (not shown)

which provides the necessary movements of the gun 12 to coat the substrate 19. When substrate 19 is a cylindrical target, for instance, for a rotating cathode magnetron, this may be rotated and the movements of the gun 12 may be simple reciprocating movements parallel to the axis of the target 19. If the substrate 19 is a flat rectangular or circular plate, the movements may be provided by a suitable robot and may be complex, e.g. including rotational cycloidal motions. For rapid deposition several guns 12 may spray the same substrate 19 at the same time.

The fuel gas for the gun 12 may be selected from one of acetylene, propylene, hydrogen or similar fuels but the present invention is not necessarily limited thereto. Particularly preferred in one embodiment of the present invention is a fuel with a lower calorific value such as one of ethylene, natural or town gas, butane or propane as these provide a lower temperature flame than acetylene and butane is particularly preferred as it gives a stable easily controllable flame and is considered safer than acetylene if powders containing copper compounds are used. It is generally accepted that oxy-acetylene flames have temperatures of 2000 °C and more. It is preferred in accordance with an embodiment of the present invention if the flame of the flame spraying gun 12 imparts a temperature only sufficient to just melt the powder to be sprayed. Temperatures of 1500 °C or less and preferably 1200 °C or less are preferred and temperatures between 600 and 1000 °C may be more preferable. These low flame temperatures minimise decomposition of the ceramic powder components during flame spraying. Moreover, they limit the impact of evaporation of the materials to be flame sprayed and allow a deposition efficiency of more than 80%, i.e. more than 80% of the solid mass originally introduced into the gun 12, becomes attached to the substrate 19. Mechanically stable, scratch resistant flame sprayed coatings are produced with these low temperatures.

The gun 12 is preferably held at 7 to 15 cm from the substrate 19 to be coated but this depends upon the size of the flame. Similar coatings have been obtained using both oxy-acetylene flame spraying and plasma spraying. Attention must be paid to the energy taken up by the sprayed particles during the spraying

and the transfer of this energy to the substrate. Intensive cooling of the substrate is preferred which may be on the side of the substrate remote from the deposited layer and/or on the same side. By altering the velocity of the particles in the flame or plasma the dwell time therein may be altered, thus limiting the energy uptake by the particles.

The material of substrate 19 preferably has a high melt temperature and a high thermal conductivity and when the substrate 19 is to be used as a target for a sputtering magnetron a good electrical conductivity is preferable. It is also preferred if the thermal expansion of the substrate material is similar to that of the ceramic coating to be applied. In accordance with embodiments of the present invention low temperature flame spraying and/or intense cooling of the substrate 19 allows the use of substrates 19 with a thermal expansion coefficient up to at least twice or down to at least a half of the thermal expansion coefficient of the ceramic coating. A non-limiting list of suitable materials may be steel, iron, stainless steel, copper or copper alloys, however the low temperature flame spraying process in accordance with the present invention, either independently or in combination with intense cryogenic cooling of the substrate 19, allows other materials to be used such as paper, cardboard or polymeric materials. Preferably, the substrate 19 should be free of grease and dry before deposition. Preferably, the outer surface of metals is sand blasted and then lapped with abrasive materials. Buffer layers between the substrate and the sprayed coating may be used such as Ni-Al or an In-alloy. These may be applied by flame or plasma spraying before application of the metal oxide coating. .

Where the substrate 19 is rigid it may be mounted in a suitable jig. For example, a cylindrical substrate 19 is preferably mounted in a rotating device such as a lathe. The substrate 19 may be held by rotatable chucks at each end thereof. The temperature of the solidified flame sprayed coating 40 on the surface of the substrate 19 is preferably measured by a temperature sensor 13, 15. The sensor head 13 is preferably a remote sensing optical head which is not in contact with the surface 40 of the flame sprayed coating. The temperature to be measured is of

the solidified coating 40 and not that of the coating immediately on impacting the substrate 19 which may have a higher temperature. Hence, the temperature sensor 13 is preferably mounted so that it lags behind the impact position of the flame sprayed materials a little. In addition a temperature sensor 31 may be provided inside the substrate 19 for further control of the deposition process. Control of deposition temperature is an important aspect of the present invention. Control of temperature affects the amount of thermal stress in the coating, a low stress reducing the possibility of cracks forming in the coating.

In accordance with one embodiment of the present invention a means for intense cooling of the substrate 19 is provided. This is preferably a cryogenic cooler comprising a supply 16 of cryogenic fluid and a delivery system 11, 14, 17, 29, 30. The delivery system may be adapted to the form of the substrate 19. For example, for a cylindrical substrate 19 the cooling device may be a conduit 17 for supplying the cryogenic fluid to a control valve 11, a conduit 30 with regularly spaced holes 29 for distribution of the cryogenic fluid inside the substrate 19 and a control device 14 for receiving the output of the temperature sensor 13, 15 and for controlling the operation of the control valve 11 so as to maintain the surface temperature of the solidified coating 40 to within a certain range. Particularly preferred is a temperature range from room temperature (25 to 30°C) to 150 °C and more preferably room temperature to 100 °C. These low temperatures avoid thermal stresses between the coating 40 and the substrate 19 providing a good bond and good coating density, hardness and scratch resistance thus helping to ensure the long term stability of such a coating. Using a cryogenic fluid such as liquid nitrogen (77 °K) is quite advantageous and economical as it does not require the complication of perfectly sealed rotating inlets and outlets to the substrate 19 when water or other liquid coolants are used. Additionally, cryogenic fluids such as liquid nitrogen produce large temperature gradients, thus increasing the thermal sink-effect. Other liquid coolants such as water are not excluded from the present invention.

The cylindrical substrate 19 may be sealed by a seal 26 at one end and with

a rotating seal 28 at the other. The seal 28 may be provided with a sealed feedthrough 27 for the supply of cryogenic fluid. If water cooling is used, rotating seals at both ends of the cylindrical substrate are considered very important to prevent escape of water vapour into the deposition environment. In accordance with an embodiment of the present invention it is preferred if the ends 26, 27 allow escape of a cryogenic fluid which then forms a shield gas around substrate 19 during the spraying process. Particularly preferred cryogenic fluids are liquid nitrogen, liquid oxygen and liquid air. With some complex ceramic materials, one or more components may be reduced in the spraying process. For such materials it may be advantageous to use a shield gas including oxygen, e.g. liquid air or liquid oxygen, which may help to reoxidise the reduced component. On the other hand with other complex ceramics it may be advantageous to reduce the contact time with oxygen at high temperatures, under which conditions liquid nitrogen would be preferred, or a reducing gas may be included such as hydrogen. It is preferable to control the atmosphere in the vicinity of the substrate 19 during coating deposition to prevent the presence of excessive water vapour and in particular to prevent condensation of water on the substrate 19. This may be achieved by generally air conditioning the air around the substrate 19 to reduce its dew point.

It is preferred if the deposition rate is selected in order to maintain the substrate surface temperatures mentioned above. Assuming the cylindrical substrate as shown in Fig. 1, the rotation speed of the substrate 19, the linear speed of the gun 12 and the rate of material exiting the gun 12 may be controlled to achieve the temperatures specified above. For instance, it has been found that when using cylindrical substrates made of stainless steel of 15 cm diameter and up to 40 cm long, a powder delivery of 5-10 g/min was suitable to produce 3 -10 mm coatings when depositing a $YBa_2Cu_3O_7$ layer. The rotational speed of the substrate 19 may be in the range 10 to 100 RPM with a surface speed in the range 1 to 40 m/min and the longitudinal feed of the gun 12 in the range 1-3 m/min, typically 2 m/min. The deposition rate per reciprocating pass of the gun 12 may be 10 to 50 micron thickness of the coating. About 10% to 15% of the deposited

coating had maintained the lattice structure of the powder and exhibited superconducting properties. It will be appreciated by the skilled person that increasing the deposition speed, deposition thickness per pass or the flame temperature or reducing the thermal conductivity of the substrate material will increase the thermal load on the cooling system and adjustments of one or more of these parameters may be necessary to obtain satisfactory coatings. The thermal conductivity of the deposited material is preferably between 1 and 5 $Wm^{-1}K^{-1}$. When deposited on a steel substrate the thermal conductivity preferably lies within the range 25 to 125 $Wm^{-1}K^{-1}$. These values are particularly preferred for $YBa_2Cu_3O_7$ coatings. Preferably, an adhesion promoter layer is applied onto the substrate before application of the coating of the metal oxide combination. The adhesion promoter may be a layer of Ni-Al or a layer of an In-alloy, for example. The deposited coating is preferably impact resistant, e.g. withstands impact of a 0.036 kg steel ball from a height of 2 metres. Preferably, about 20% or up to 30% of a noble metal is included in the oxide material to improve electrical and thermal properties of the deposited layer. The noble metal is preferably silver. The noble metal may in included as a salt or oxide, e.g. silver nitrate or silver oxide, in the material to be sprayed. Preferably, the electrical resistivity of the deposited layer is lower than 15 x $10^{-6}$ Ohm.m, more preferably lower than 10 x $10^{-6}$ and most preferably less than 5 x $10^{-6}$ Ohm.m. Values below 1 x $10^{-6}$ Ohm.m can be achieved. Up to 30% of a noble metal such as silver may be added to lower the resistivity. These values are particularly preferred for $YBa_2Cu_3O_7$ coatings.

Fig. 2 is a schematic representation of a further embodiment of the flame spraying process and apparatus in accordance with the present invention. Components in Fig. 2 with the same reference numbers as in Fig. 1 refer to equivalent items. The substrate 19 in accordance with this embodiment is a foil or sheet of metal, plastic or other flexible material which is wound from a pay-off spool 32 to a take-up spool 36. Where the final coating 40 cannot be spooled, the foil with coating 14 may be drawn linearly from the pay-off spool 32 and cut into lengths. The coating 40, which may be a superconducting layer, is flame sprayed

with a flame spray gun 12 similar to the one described with respect to Fig. 1. In particular it is preferable to use a fuel with a lower calorific value than acetylene such as natural or town gas, butane or propane. Preferably, the temperature of the flame of the gun 12 imparts a temperature of 1500 °C or less, more preferably 1200 °C or less to the material being sprayed through the flame. This material may be in the form of powder either of finished components of the coating 40, e.g. oxides, or precursors thereof, e.g. nitrates, or may be in the form of a slurry of powders, e.g. oxides, or a solution, e.g. of nitrates. Gun 12 may be controlled by hand or more preferably by a robot to provide zigzag motions across the width of foil 19 thus applying an even coating 40. Preferably a layer of 10 to 50 micron thickness is applied in each pass.

The temperature of the coating 40 may be monitored by one or more optical sensors 13, 15. The temperature of the foil 19 is regulated by means of a cryogenic fluid supplied from a container 16 to a series of holes or jets 29 via conduit 17, a controllable valve 11 and a conduit 30. The valve 11 is controlled by a controller 14 to maintain the temperature of the foil as determined by the sensor 13, 15 to less than 400 °C, preferably less than 150 °C and most preferably between 50 and 100 °C. Such low temperatures allow a wide range of materials for substrate 19 including polymeric materials, cellulosic materials as well as metals. Although only one controller 14 is shown the present invention includes several controllers each with its own controllable cryogenic cooling device 11, 29, 30 for individually controlling the temperature of different parts of the foil 19 or coating 40. Optionally, an optical encoder 34 may be attached to a roller 35. The optical encoder may be read with an optical sensor 37, 38, the pulse frequency generated in the sensor 37, 38 being proportional to the linear speed of the foil 19. This value may also be used by the controller 14 to control the complete process to maintain the temperatures and coating thicknesses mentioned above.

When producing superconducting coatings 40, it is preferred if there is no condensation of water onto the coating 40 nor onto the foil 19 so it is preferred if the atmosphere around the deposition equipment is air conditioned to reduce the

dew point to below ambient temperature. Preferably the coated substrates in accordance with this invention are preferably stored for long periods in a plastic bag filled with a dry inert gas such as dry nitrogen. One aspect of the present invention is the flame spraying of powders which already have superconducting properties in the powder form. Using the methods in accordance with the present invention it is possible to flame spray such coatings and retain 10% to 15% of superconducting property of the coating 40 produced without extensive post-heat treatments.

The superconducting and/or ceramic powder and/or metallic powder to be used for flame spraying is preferably homogeneous, exhibits the appropriate rheological properties and correct stoichiometry to generate the required properties in the final coating. Typical preferred densities for superconducting powders may lie in the range 4 to 5 g/cm$^3$. A non-limiting list of suitable materials which may be flame sprayed as powders, slurries or liquid solutions in accordance with the present invention are: superconducting materials such as $R_1Ba_2Cu_3O_y$ where R is Y, La, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, Lu; or $Bi_{2-x}Pb_xSr_2Ca_{n-1}Cu_nO_y$, $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+3}$, $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$; or $Ba_2Ca_{n-1}O_{2n+2}$, or $CaBa_2Ca_{n-1}Cu_nO_{2n+\delta}$; or cuprate high temperature superconductors of the general formula $A_mE_2R_{n-1}Cu_nO_{2n+m+2}$ where A, E, R are selected from various cations such as A= Bi, Tl, Hg, Pb, Cu or a lanthanide element, E = Ba or Sr and R = Ca or rare earth element; or piezo-electric ceramics, for example, with the general formula $M(Zr_xTi_{1-x})O_3$ where M = Pb, Ba or Sr; or refractory ceramic oxides, nitrides, carbides or phosphates, e.g. $Al_2O_3$, MgO, $Zr_xO_y$; or metals and their alloys.

In accordance with a further embodiment of the present invention a method is provided for production of suitable ceramic powders. By starting from aqueous solutions containing the salts of the metals in the correct proportions a reactive precursor powder can be obtained using commercially available spray drying equipment in batches of kilograms. The type of salt (mostly nitrates) should preferably be compatible with thermal decomposition to oxides in further

processes such as sintering or flame spraying. In accordance with the present invention spray dried nitrate powders may be flame sprayed directly or the powders may first be sintered and then flame sprayed.

A spray drying system 50 in accordance with an embodiment of the present invention for the delivery of powder suitable for subsequent flame spraying is shown schematically in Fig. 3. The input liquid is drawn from a suitable source 53 via a peristaltic pump 54 to a spray head 71. Pressurised air 51 is drawn in through an air dryer and optional pre-heater 52 to the spray head 71 by a suction device such as a fan 63 at the end of the generally closed system. The liquid from source 53 enters the spray head 71 which is cooled by any suitable means 55 to prevent clogging due to early evaporation of the liquid. The liquid is atomised in a co-current two fluid nozzle 71 by the dry pressurised air 51 and discharged it into a chamber 56 where it dries to a powder. The liquid from source 53 may be a solution of suitable nitrates or a slurry of the relevant oxides with the addition of other agents such as binders.

Air 65 is drawn in by fan 63 over a heater 64 and introduced into chamber 56 via a ring orifice 72 which surrounds the outlet of the spray head 71. The air 65 also heats the spray head 71. The circumferential air flow 65 guides the evaporating liquid in chamber 56 and helps to prevent the powder sticking to the walls of the chamber 56. The air throughput of fan 63 is chosen so that powder of the correct grain size is swept from chamber 36 through an optional heater section 58 into a powder collector 59. Heavier particles settle out in trap 57 and are removed from the bottom of chamber 56.

The powder collector 59 may be any suitable device such as a cyclone, a bag filter or an electrostatic filter although a cyclone is preferred. The cyclone discharges the powder into a removable container 60 sealed to the bottom of the cyclone 59. Spent air is removed via the trap 61 and scrubbed in scrubber 12 to remove impurities. The final clean air is exhausted to atmosphere by the fan 63 which controls air flow through the system.

The control system 66 - 70 for the process functions as follows. The

rotational speed of the centrifugal air pump 53, the temperature of the heating element 64 and the flow of the atomised air are set with controller 67, 70. Air flow is measured by gauge 68. The temperature of the hot air 65 and the air in the tube leading from the chamber 56 to the optional heater 58 is monitored using thermocouples 66, whereas final powder temperature is monitored by temperature sensor 69.

After spray drying, the powder may be sintered in a single step. For example, to produce a superconducting powder of the general formula $YBa_2Cu_3O_7$ with optional Ag, the required nitrates are dissolved in water in the correct stoichiometric proportions and spray dried as indicated above. The nitrates are then reduced to oxides by sintering at 920 - 960 °C for 40 to 60 hours. Optionally the nitrates may first be reduced by heating in air at 780 °C for 10 hours before sintering at the above temperatures and times. The $YBa_2Cu_3O_7$ powder produced by this procedure is superconducting. On aspect of the present invention is to produce powders with superconducting properties by spray drying and optional sintering and then to flame spray these superconductive powders at the lowest flame temperatures necessary to obtain melting of the powder and coating formation on the substrate while cooling the coating in the fastest possible way. By this procedure the crystal structure present in the superconducting powder is disturbed as little as possible by the flame spraying process. Of course, melting the powder during flame spraying causes complete loss of crystal organisation if the time in the melt is long. By lowering the flame temperature and shortening the time in the melt phase by cooling the coating very rapidly in accordance with the present invention, some local crystal organisation is kept in the final flame sprayed coating, e.g. about 10% of the final coating is in the superconducting phase, thus providing a coating on the substrate with an optimum starting condition for further heat processing to develop full superconducting properties. The addition of the metallic silver enhances the thermal and mechanical properties in later flame spraying and magnetron sputtering.

Alternatively, the powder for flame spraying may be spray dried from

slurries of the relevant oxides in the correct stoichiometric proportions with the optional addition of silver in the above apparatus in accordance with the present invention. For instance, in the manufacture of a ceramic material the mixture of oxides may be produced by individually sieving them to 40 micron and then mixing in the correct proportions to obtain the stoichiometric proportions in the final coating. A quantity of deionised water is added of about 60% by weight of the powder as well as a quantity of an organic binder such as PVA (polyvinyl acetate) equal to about 2% by weight of the powder and then mixed into a slurry. The slurry is then spray dried as described above resulting in powder with a grain size from 30 to 50 micron. Generally, spray dried oxide slurries do not require sintering before flame spraying. The organic binder may be burnt out during flame spraying or in a special sintering step.

Spray drying of 10% by weight nitrate solutions generally produce grain sizes of 3 micron on average with at least 90% of the grains between 0.5 and 5 microns. In order to obtain the required grain size it is preferable to sinter as mentioned above. Light grinding and sieving of this sintered powder may produce a mass fraction of more than 80% with grain sizes between 40 and 80 micron. By the variation of appropriate concentrations of the solution of the aqueous media 53, and/or the addition of binders and/or the spray drying of slurries rather than solutions, allows control of the grain size in the final powder to between 2 and 100 microns. For example, the present invention includes the addition of organic binders such as polyvinyl acetate (PVA) to the liquid to be spray dried to control grain size in the final powder. Such binders may be burnt out in a later high temperature process such as sintering. An average grain size of 40 to 80 microns is preferred for good flame spray deposition. The final powder may be lightly milled and sieved to be improve the homogeneity of grain sizes.

One aspect of the present invention is the inclusion of silver metal in the final superconducting ceramic coating. This is achieved as mentioned above by inclusion of about 20% to 30% by weight of the ceramic materials of silver nitrate when nitrate solutions are spray dried and the flame sprayed or by addition of

$Ag_2O$ powder in an oxide slurry which is then spray dried and flame sprayed. The addition of silver in the flame sprayed material is beneficial for the inter-grain adhesion and heat dispersal during flame spraying thus yielding a strong and dense coating. The silver improves the thermal and electrical conductivity of the flame sprayed coating which is beneficial to the sputtering process when the substrate is used as a sputtering target. The improved conductivities allow higher power throughput for the magnetron than targets not containing silver.

The flame spraying process in accordance with the present invention allows the reconditioning of targets for sputtering magnetrons. It is well known that the presence of a static race-track plasma on a magnetron target during sputtering results in an erosion groove and poor target utilisation. Using the flame spraying process of the present invention such a worn target may be reconditioned by spraying the appropriate target material into the erosion groove and building up the target to its former thickness in these regions. By providing the intensive cryogenic cooling described above, the general target temperature may be kept below 400 °C, preferably below 150°C and most preferably between room temperature (~25°C) and 100°C. These low temperatures result in little damage to the existing target material while still providing a mechanically strong coating in the old erosion grooves. Such as process is particularly economic when the target material is expensive such as superconducting materials. The flame spraying gun 12 described above may be hand held and the contour of the erosion groove in the used target followed building up the lost material slowly, preferably 10 to 50 micron per pass. Preferably the gun 12 is controlled by a robot which is programmed to execute the correct motions with the gun 12 to fill up the erosion groove in the target.

While the invention has been shown and described with reference to preferred embodiments, it will be understood by those skilled in the art that various changes or modifications in form and detail may be made without departing from the scope and spirit of this invention as defined in the attached claims.

## CLAIMS

1. A composite comprising: a substrate and a coating deposited on said substrate, the coating being deposited by spraying, the thickness of the coating being at least 5 mm, more preferably greater than 8mm, the coating comprising metal oxides.

2. The composite according to claim 1, wherein the coating comprises a superconductor precursor and at least 10% of the coating is in a superconductive phase

3. The composite according to claim 1 or 2, wherein the composite is a target for a sputtering magnetron.

4. The composite according to claim 3, wherein the target is cylindrical.

5. The target for a sputtering magnetron comprising: a cylindrical substrate and a coating deposited on said substrate, the coating being deposited by spraying, the thickness of the coating being at least 3mm, more preferably at least 5 mm, most preferably greater than 8mm, the coating comprising a superconductor precursor and at least 10% of the coating is in a superconductive phase.

6. The target or a composite in accordance with any previous claim, wherein the coating has a thermal conductivity of between 1 and 5 $Wm^{-1}K^{-1}$.

7. The target or a composite in accordance with any previous claim, wherein the thermal conductivity of the composite or the target through the substrate and the coating is in the range 25 to 125 $Wm^{-1}K^{-1}$.

8. The target or a composite in accordance with any previous claim, wherein the coating has an electrical resistivity of lower than $15 \times 10^{-6}$ Ohm.m, more preferably lower than $10 \times 10^{-6}$ and most preferably less than $5 \times 10^{-6}$ Ohm.m.

9. The target or a composite in accordance with any previous claim, wherein the coating can withstand impact of a 0.036 kg steel ball from a height of 1 metre, preferably from 1.5 metre.

10. The target or a composite in accordance with any previous claim, wherein the spraying is one of plasma spraying and flame spraying.

11. A method of depositing by spraying a superconductor precursor layer onto a cylindrical target for a sputtering magnetron, the layer having a thickness of at least 3 mm, and at least 10% of the layer being in a superconductive phase.

12. A method of depositing by spraying a layer onto a substrate, the layer having a thickness of at least 5 mm, and the coating comprising metal oxides.

13. The method according to claim 11 or 12, wherein the spraying step is one of flame spraying and low-pressure or atmospheric pressure plasma spraying.

14. The method according to claim 13, wherein the spraying step includes spraying a material through a spraying head, the material being in the form of a powder, a slurry or a solution.

15. A method of reconditioning a used target for a sputtering magnetron having an erosion groove in the target material, comprising the step of: flame or atmospheric pressure plasma spraying target material into the erosion groove.

16. A reconditioned target for a sputtering magnetron, comprising:
an erosion groove in the target material; and target material flame sprayed or atmospheric plasma sprayed into said groove to restore the thickness of the target material to that of the unused material.

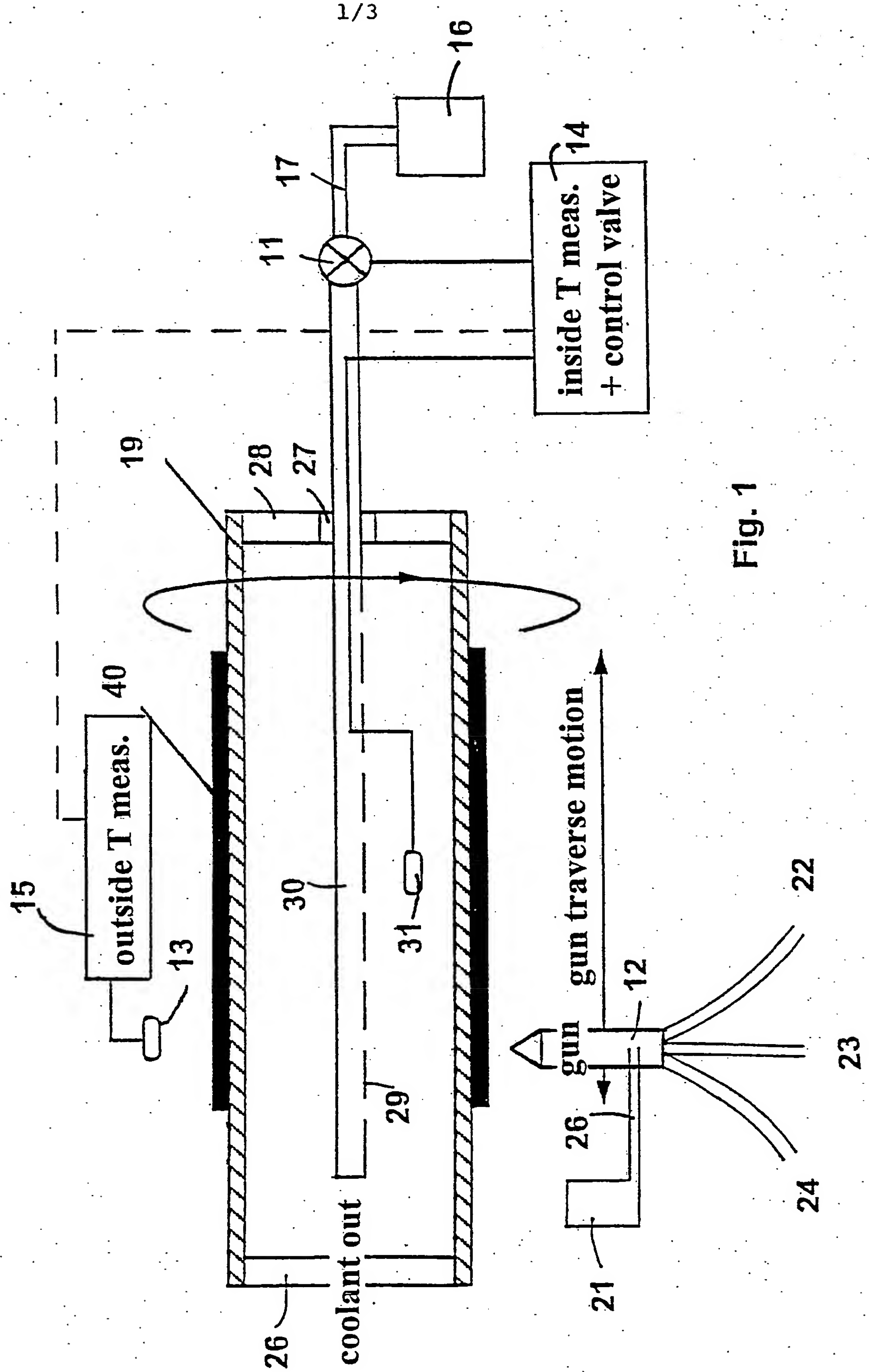
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Fig. 1

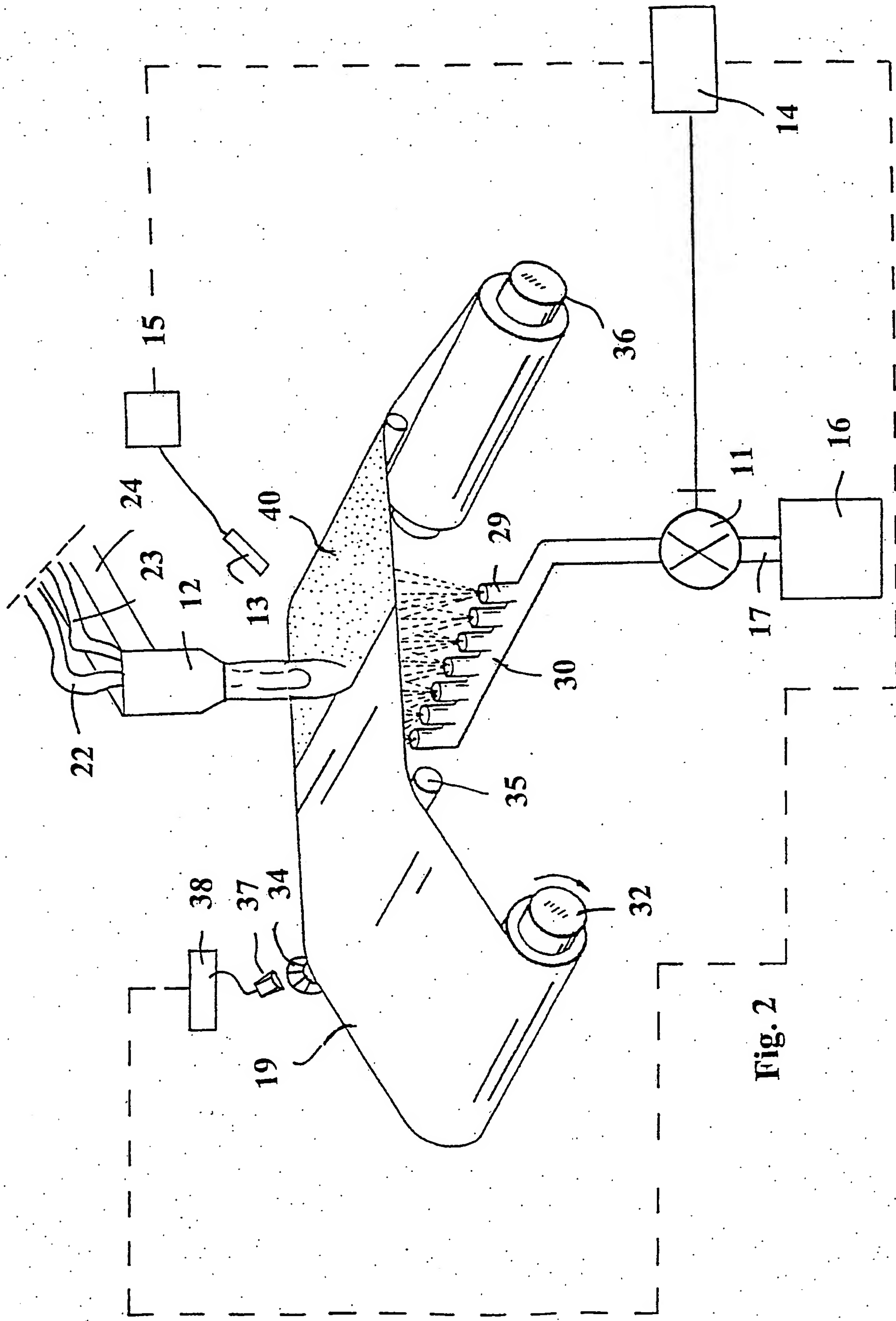


Fig. 2

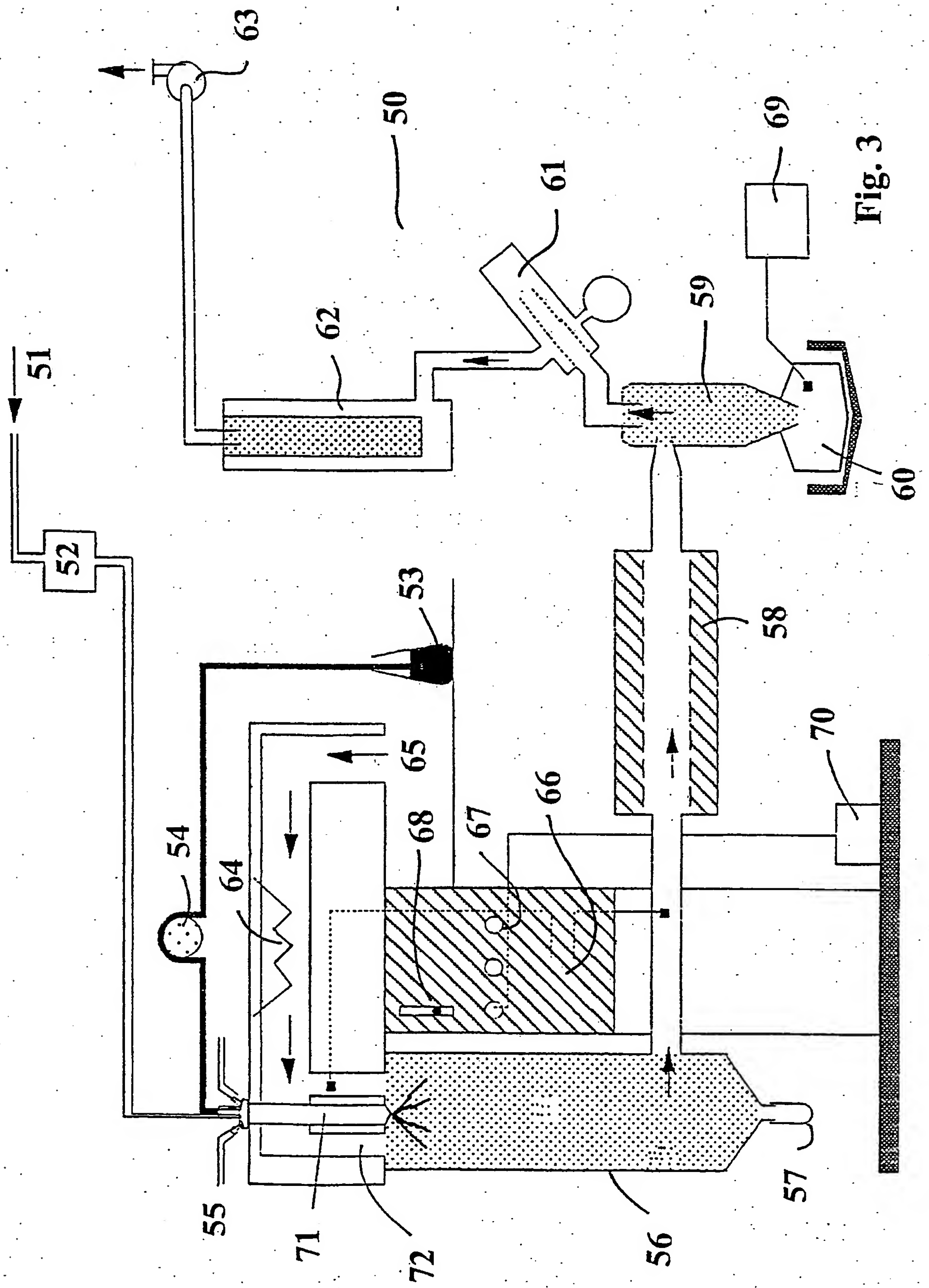


Fig. 3

# INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 99/03599

**A. CLASSIFICATION OF SUBJECT MATTER**
IPC 6 C23C4/10 C23C4/12 C23C14/34

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | US 5 196 400 A (CHEN CHIOU T ET AL) 23 March 1993 (1993-03-23) cited in the application column 3, line 52 - column 4, line 16 | 1-5, 10-14 |
| X | EP 0 330 196 A (PERKIN ELMER CORP) 30 August 1989 (1989-08-30) page 5, line 20 - line 25; claims 1,8 | 1,2,10, 12-14 |
| X | CH 648 358 A (CASTOLIN SA) 15 March 1985 (1985-03-15) claim 1 | 1,10, 12-14 |
| X | DD 277 471 A (MANSFELD KOMBINAT W PIECK VEB) 4 April 1990 (1990-04-04) page 2, line 21 - line 23 | 15,16 |

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
"&" document member of the same patent family

| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 9 September 1999 | 16/09/1999 |

| Name and mailing address of the ISA | Authorized officer |
|---|---|
| European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,<br>Fax: (+31-70) 340-3016 | Patterson, A |

2

## INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 99/03599

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | DE 40 15 387 A (LEYBOLD AG)<br>21 November 1991 (1991-11-21)<br>the whole document | 15,16 |
| A | EP 0 377 073 A (MITSUBISHI METAL CORP)<br>11 July 1990 (1990-07-11)<br>page 3, line 41 - line 57; table 2<br>page 7, line 7 - line 23; table 4 | 5-8 |

2

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

## INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP 99/03599

**Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)**

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 9
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
SEE FURTHER INFORMATION SHEET

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

**Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows:

SEE FURTHER INFORMATION SHEET

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☒ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

**Remark on Protest**

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

# INTERNATIONAL SEARCH REPORT

International Application No. PCT/EP 99/03599

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1-8,10-14

   Claims for a composite comprising an oxide-containing coating deposited by spraying and having a certain minimum thickness, a sputter target having a layer of a superconductor precursor, also deposited by spraying and having a minimum thickness, and methods for producing each of these products, respectively.

2. Claims: 15,16

   Reconditioned sputter target and method for its manufacture by flame or plasma spraying material into the sputtered erosion groove.

The only common concept linking subjects 1 and 2 is the application of spraying for depositing layers of material. Since this feature is known from many prior art documents (see for example search report) there is effectively no common concept to connect the two groups of claims. Furthermore, while subject 1 addresses the problem of producing relatively thick deposits of oxides by means of spraying, subject 2 solves the unrelated problem of spraying an unspecified material to repair local damage on a target.

Therefore there is a lack of unity between the two subjects.

Nevertheless, since the EPO has already searched the subject-matter of claims 15 and 16 in connection with the priority application EP98870120, an International search report is issued for both subjects.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 9

Claim 9 relates to a product defined (inter alia) by reference to the following parameter:
the result of a test involving impact of a ball consisting of an unspecified steel, wherein both the weight of the ball and the height from which it is dropped are arbitrarily chosen.
The use of this parameter in the present context is considered to lead to a lack of clarity within the meaning of Article 6 PCT. It is impossible to compare the parameter the applicant has chosen to employ with what is set out in the prior art. The lack of clarity is such as to render a meaningful complete search impossible. Consequently, the search has been restricted to the remaining claims

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP 99/03599

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---|---|---|
| US 5196400 A | 23-03-1993 | NONE | |
| EP 0330196 A | 30-08-1989 | CN 1036286 A<br>JP 1309952 A | 11-10-1989<br>14-12-1989 |
| CH 648358 A | 15-03-1985 | NONE | |
| DD 277471 A | 04-04-1990 | NONE | |
| DE 4015387 A | 21-11-1991 | NONE | |
| EP 0377073 A | 11-07-1990 | JP 2156079 A<br>JP 2157150 A<br>KR 9507087 B<br>US 5077269 A<br>KR 9507088 B | 15-06-1990<br>15-06-1990<br>30-06-1995<br>31-12-1991<br>30-06-1995 |